

PHOTOCHEMISTRY OF NITRAMINES II
STOICHIOMETRY, INTERMEDIATES AND PRODUCTS

Harry Whittaker

United States Naval Postgraduate School



THESIS

PHOTOCHEMISTRY OF NITRAMINES II
STOICHIOMETRY, INTERMEDIATES AND PRODUCTS

by

Harry Whittaker

Thesis Advisor:

Charles F. Rowell

June 1971

Approved for public release; distribution unlimited.

T139436

LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY, CALIF. 93940

Photochemistry of Nitramines II
Stoichiometry, Intermediates and Products

by

Harry Whittaker
Lieutenant (Navy), Canadian Forces
B. Eng., (Chem. Eng.), Royal Military College, 1963

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the
NAVAL POSTGRADUATE SCHOOL
June 1971

178515
W564
c 1

ABSTRACT

This investigation was concerned with the photochemical decomposition of nitramines, particularly N-nitropyrrolidine and N,N-dinitropiperazine. Photolyses were carried out in solution and in the solid state. Intermediates were identified by spectroscopic studies and by synthesis.

On the basis of the intermediates, products, and spectroscopy of products, a mechanism for the photochemical decomposition of N-nitropyrrolidine was postulated.

TABLE OF CONTENTS

I.	INTRODUCTION	-----	8
II.	HISTORICAL	-----	9
III.	EXPERIMENTAL	-----	14
A.	SYNTHESIS	-----	14
1.	Piperazine Dihydrochloride	-----	14
2.	N,N-Dinitropiperazine	-----	14
3.	N-Formylpyrrolidine	-----	15
4.	N-Nitropyrrolidine	-----	15
5.	2-Pyrrolidone	-----	16
6.	N-Hydroxypyrrolidine	-----	17
7.	Succinic Anhydride	-----	17
8.	N-Hydroxysuccinimide	-----	18
9.	Δ -1-Pyrroline-Oxide	-----	19
B.	ELECTRON SPIN RESONANCE STUDIES	-----	20
1.	Dinitropiperazine	-----	20
2.	RDX	-----	20
3.	HMX	-----	21
4.	N-Nitropyrrolidine	-----	21
5.	N-Hydroxysuccinimide	-----	21
C.	MASS SPECTRAL STUDIES	-----	21
1.	Dinitropiperazine	-----	21
2.	N-Nitropyrrolidine	-----	22

3.	N-Nitropiperidine -----	23
4.	4-Methyl-1-Nitropiperidine -----	24
5.	N-Hydroxypyrrolidine/NO -----	24
D.	KINETIC STUDIES OF PHOTOLYSIS OF NITROPYRROLIDINE -----	25
1.	Nitropyrrolidine in n-Heptane -----	25
2.	Nitropyrrolidine/Acrylonitrile -----	25
E.	ATTEMPTED ADDUCT FORMATION -----	25
1.	Photo-adduct of Photolysis Products of N-Nitropyrrolidine and Acrylonitrile -----	25
2.	Dark Phase Adduct of Photolysed Dinitropiperazine and Acrylonitrile -----	28
3.	Dark Phase Adduct of Photolysed N-Nitropyrrolidine and Acrylonitrile -----	29
F.	NUCLEAR MAGNETIC RESONANCE SPECTROMETRY STUDIES OF SUSPECTED INTERMEDIATES -----	30
G.	GASEOUS INFRA-RED ABSORPTION STUDY -----	30
H.	THERMAL SENSITIVITY OF N,N-DINITROPIPERAZINE ---	31
I.	IMPACT SENSITIVITY -----	31
IV.	RESULTS -----	34
A.	ELECTRON SPIN RESONANCE STUDIES -----	34
B.	MASS SPECTRAL STUDIES -----	38
C.	KINETIC STUDIES -----	57
D.	ATTEMPTED ADDUCT FORMATION -----	62

E.	NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	
	STUDIES OF SUSPECTED INTERMEDIATES -----	64
F.	INFRARED SPECTRUM OF THE GASEOUS PHOTOLYSIS	
	PRODUCTS OF DINITROPIPERAZINE -----	67
G.	THERMAL SENSITIVITY OF DINITROPIPERAZINE -----	67
H.	IMPACT SENSITIVITY -----	67
I.	NON-GASEOUS PHOTOLYSIS PRODUCT	
	IDENTIFICATION -----	67
V.	DISCUSSION -----	71
	BIBLIOGRAPHY -----	79
	INITIAL DISTRIBUTION LIST -----	83
	FORM DD 1473 -----	84

LIST OF TABLES

	Page
I. Thermal Decomposition Products of HMX and RDX -----	9
II. Appearance of Solution During Photolysis: N-Nitropyrrolidine in Acrylonitrile -----	26
III. Mass Spectra of Gaseous Products (at Very Low Pressures) of Photolysis of N,N-Dinitropiperazine -----	43
IV. Mass Spectra of Very Low Pressure Gaseous Photolysis Products of N-Nitropyrrolidine -----	46
V. Mass Spectra of Very Low Pressure Gaseous Products of Photolysis of N-Nitropyrrolidine. Low Temperature Fractionation Attempted. -----	49
VI. Mass Spectra of Very Low Pressure Gaseous Photolysis Products of N-Nitropiperidine -----	52
VII. Mass Spectra of Very Low Pressure Gaseous Photolysis Products of 4-Methyl-N-Nitropiperidine -----	54
VIII. Mass Spectrum of Very Low Pressure Gaseous Products of Photolysis of N-Hydroxypyrrolidine in the Presence of NO. -----	55

LIST OF DRAWINGS

		Page
1.	Electron Spin Resonance Spectrum from Photolysis of N,N-Dinitropiperazine in Dimethylformamide -----	35
2.	Electron Spin Resonance Signal from Photolysis of N,N-Dinitropiperazine Solid Powder -----	36
3.	Electron Spin Resonance Signal from Photolysis of RDX Solid Powder -----	37
4.	Electron Spin Resonance Signal from Photolysis of HMX Solid Powder -----	39
5.	Electron Spin Resonance Signal from Photolysis of N-Hydroxysuccinimide in DPCC -----	40
6.	Electron Spin Resonance Signal from Photolysis of N-Nitropyrrolidine in DPCC -----	41
7.	Ultraviolet Absorbance vs. Photolysis Time for N-Nitropyrrolidine in n-Heptane -----	57
8.	Ultraviolet Absorbance vs. Photolysis Time for N-Nitropyrrolidine in n-Heptane -----	58
9.	Ultraviolet Absorbance vs. Photolysis Time for N-Nitropyrrolidine and Acrylonitrile in n-Heptane -----	59
10.	Ultraviolet Absorbance vs. Photolysis Time for N-Nitropyrrolidine and Acrylonitrile in n-Heptane -----	60
11.	Ultraviolet Absorbance vs. Photolysis Time for N-Hydroxypyrrolidine in n-Hexane -----	61
12.	NMR Spectrum of Dark Phase Adduct of Photolysed Dinitropiperazine and Acrylonitrile -----	65
13.	Thermal Stability of N,N-Dinitropiperazine -----	68
14.	Infra-Red Spectrum of X : 4000-1300 cm ⁻¹ -----	69
15.	Infra-Red Spectrum of X : 1300-400 cm ⁻¹ -----	70

I. INTRODUCTION

The nitramines are a class of compounds which contain the group N-NO_2 . Most of these compounds are potentially explosive and, in fact, RDX and HMX, two members of this class, are commonly used in military explosives. In spite of this, very few studies have been made on the nitramines.

The thermal sensitivity and decomposition of RDX and HMX are the most studied aspects of this class. Almost no published work exists on the photolysis of these compounds. What has been done leaves the mechanism of photochemical decomposition open to question.

RDX and HMX are relatively complex compounds containing several N-NO_2 groups. It was therefore decided to study more simple members of the class in an effort to elucidate the mechanism of photochemical decomposition.

II. HISTORICAL

Because of their potential and, in some cases, use as military explosives, the thermal stability of nitramines has been the subject of some recent studies. Differential thermal analysis studies on nitramines was carried out by Carignan and Satriana [1] All but three of the nitramines studied by them decomposed at high temperatures but no clear relation between structure and the decomposition temperature could be detected. No attempt was made to identify the products of decomposition.

Several studies on the thermal decomposition of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) have been carried out. The percentage of products of decomposition as measured by mass spectrometry are listed in Table I.

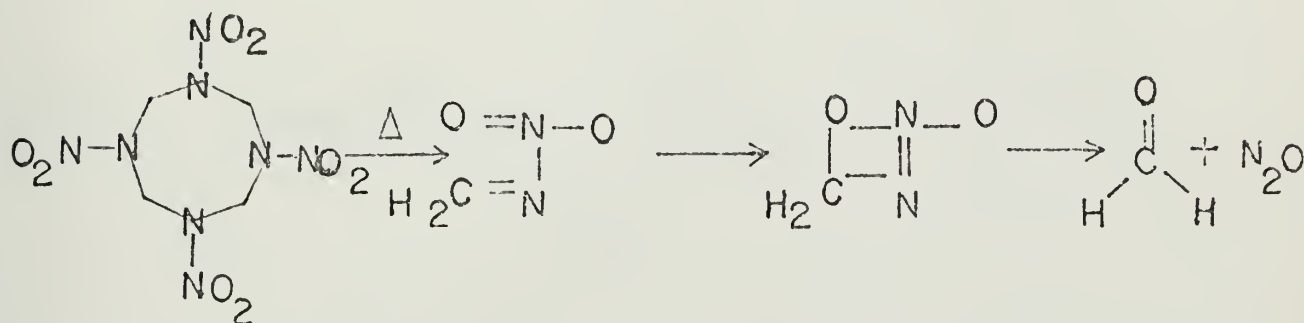
TABLE I

Investigator Nitramine	Suryanarayana [2]	Maksinov [3]	Robertson [4]	
				^b
N ₂ O	HMX	HMX	HMX	RDX
NO	40		38.5	14.0
N ₂	9.9			
HCN	9.6	major ^a	16.6	17.2
CH ₂ O	4.5		18.5	34.4
CO ₂	8.5			
CO	8.5	major ^a	present ^a	present ^a
H ₂	4.1		9.4	22.4
H ₂ O			16.4	11.8
				0.2
			present ^a	present ^a

a. In those areas marked "major," or "present," the quantity was not reported.

b. Robertson reported "considerable solid residue" from the thermal decomposition.

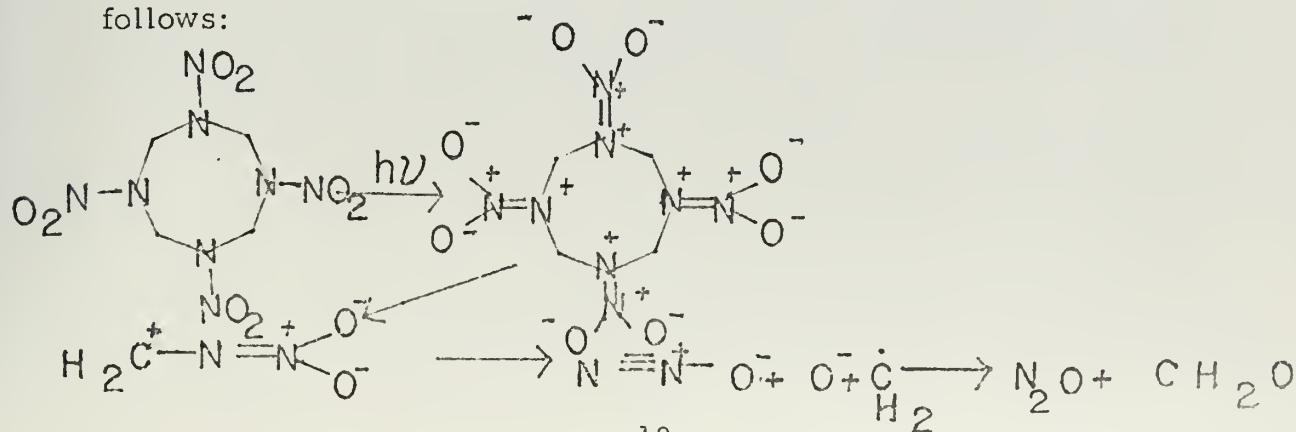
Based on N-15 tracer studies, Surayanarayana proposed the following mechanism for the thermal decomposition of HMX.



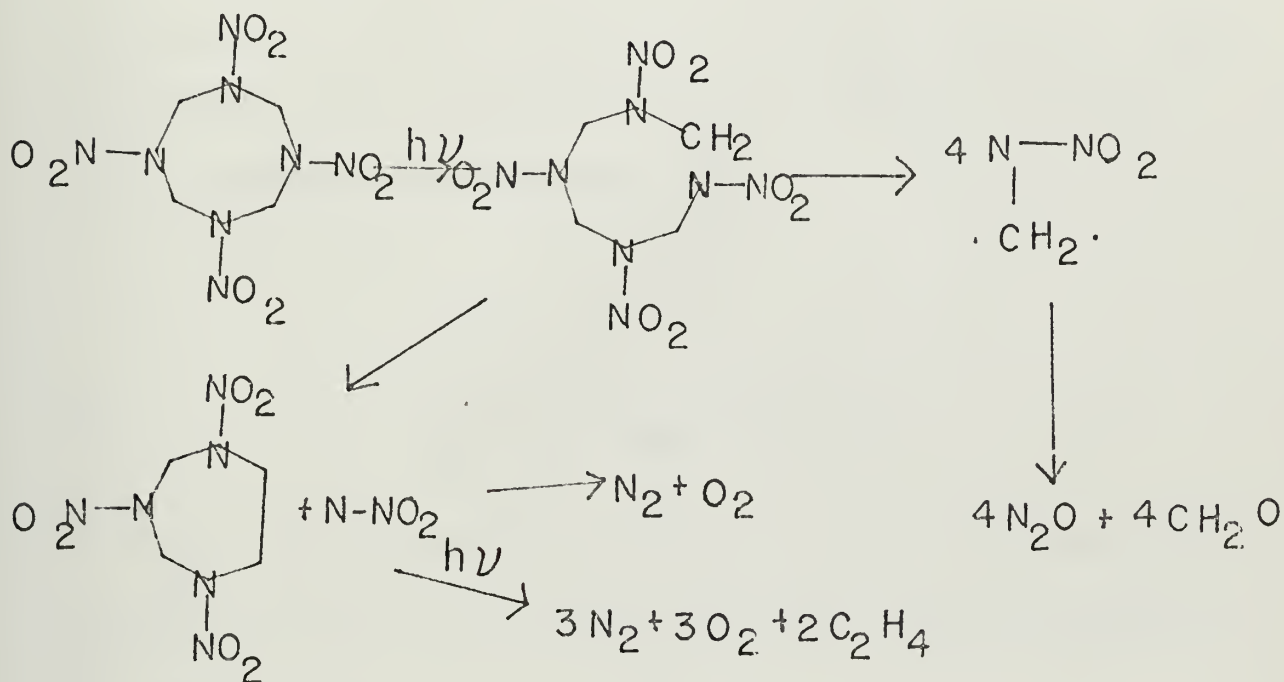
In studies on the thermal decomposition products of dimethylnitramine, Flournoy [5] was able to establish that the overall reaction was first order and unaffected by the addition of NO.

In 1967, Suryanarayana [6] reported that the ultraviolet photolysis of HMX caused the solid state transitions to occur at reduced temperatures. No photolysis products were reported. The first mechanism for the photolysis of HMX was suggested by Maycock [7]. His mechanism which supported his major gaseous products N_2 and CH_2O was as

follows:



Torbit [8] found that the photolysis products varied with the conditions of photolysis. Thus, in acetone solution the products were N_2 , C_2H_2 , O_2 , CO_2 , and N_2O ; for the solid vacuo, N_2 , C_2H_2 , C_2H_4 , CH_2O , and N_2O . The mechanism proposed to account for these products is shown below:

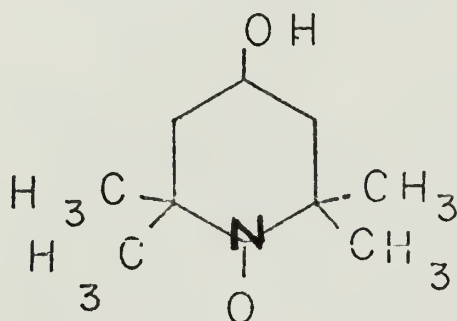


A solid photolysis residue was also reported but no attempt at classification was made.

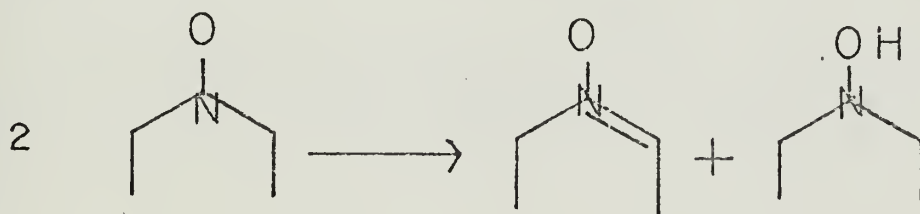
A study on the photolysis of RDX in acetonitrile was carried out by Darnez [9]. They reported that a radical was visible in the esr spectrum of the solution during irradiation. No attempt was made to identify the radical or the irradiation products.

Cyclic Nitroxides

Cyclic nitroxides of the type $\text{RC}_2\text{N}(\text{O})\text{CR}_2$ have been obtained during the photolysis of the parent hydroxylamines [10]. In the cases where $\text{R}=\text{H}$, the radicals have been short-lived intermediates which could only be detected by ESR techniques. If, however, alkyl groups are substituted for R, the stability increases markedly. 2,2,6,6-tetramethyl-4-piperidinol N-oxide (I), for instance, can be recrystallized and stored. It undergoes reactions quite independent of the radical [11] and its mass spectrum has been determined. [12]

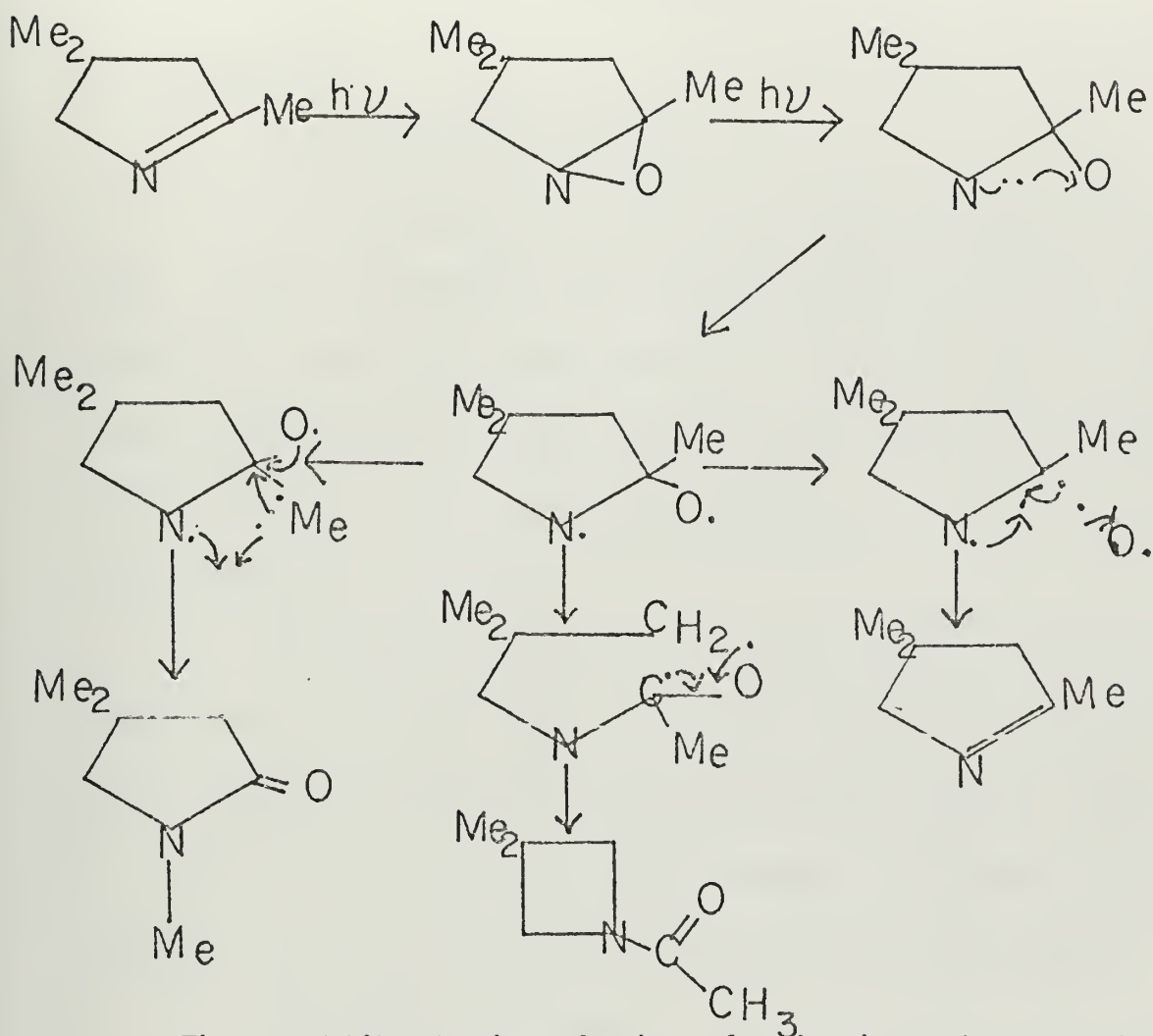


The mechanism for decay of nitroxides having a β -hydrogen has been proposed [13] as a bimolecular mechanism giving the nitron and the hydroxylamine.



The ability of the nitroxide to abstract a proton has been proven by Keana [14] in the case of 4-hydroxy-2,2,6,6-tetramethyl-1-oxyl. It has been shown by Kaminsky and Lamchen [15] and others, that the photolysis of cyclic nitrones gives oxaziridines. Kaminsky and Lamchen also found other products upon further photolysis of the oxaziridine.

The mechanisms which they propose in the case of 2,4,4-trimethyl-1-pyrroline is as follows:



The oxaziridine ion has also been found to be an important intermediate in the mass spectral fragmentation of nitrones [16].

III. EXPERIMENTAL

A. SYNTHESIS

1. Piperazine Dihydrochloride

This preparation was adapted from that of George and Wright [17]. 11.0 g. of piperazine (anhydrous) were placed in a 150 ml flask. 50 ml of H_2O were added and the solution was stirred until the majority of the piperazine had dissolved. 50 ml of concentrated (12.1 M) HCl was added slowly causing the reaction mixture to heat and the remainder of the piperazine to dissolve.

The liquid was evaporated at reduced pressure and the solid residue was dissolved in a small amount of boiling H_2O , cooled slowly to $0^{\circ}C$, and then reprecipitated by addition of 100% ethanol. A yield of 15.0 g (61%) of shiny white needles was obtained. The melting point obtained, $318^{\circ}C$, agreed with that obtained by George and Wright.

2. N,N-Dinitropiperazine

This preparation was adapted from that of George and Wright [17] .

In a round bottom 3-neck flask was mixed 15 ml of Red Fuming Nitric acid, 20 ml acetic anhydride, and 15 ml acetic acid. The acid solution was kept under nitrogen provided at just over atmospheric pressure from a tank to the flask through an adapter fitted to one neck of the flask. The flask was kept stirred in an ice-water bath and 5.1 g. of piperazine dihydrochloride was added during 25 minutes, the

temperature never being allowed to exceed 10°C. After one-half hour of stirring at 0-5°C, the solution was stirred at room temperature for 74 hours. At the end of this time, 35 ml of H₂O was added and the liquid was then removed at reduced pressure. The crude product, yield 5.2 g (92.3%) was recrystallized from acetic acid and then recrystallized twice more from boiling water. The final yield was 4.7 g (83.4%) of shiny needles which melted at 216-217°C. George and Wright reported a melting point of 214.8-216°C.

3. N-Formylpyrrolidine

This preparation was adapted from that of Coburn and Ungnade [18] .

30 ml of pyrrolidine was refluxed for 2 hours with 16 ml of 97% formic acid. The reaction mixture was distilled, the N-formylpyrrolidine being collected at 155°C at a pressure of 25 Torr.

The yield was 13.4 g (52%) of N-formylpyrrolidine, a colorless liquid.

4. N-Nitropyrrolidine

This preparation was adapted from that of Coburn and Ungnade [18] .

50 ml of trifluoroacetic acid and 50 ml of acetic anhydride were cooled to 0°C in a round bottom flask. The solution was kept at a temperature of less than 3°C by a salt-ice-water bath while 35 ml of red fuming nitric acid was added with stirring. 13.4 g of N-formylpyrrolidine was added over a one-half hour period. The temperature was not allowed to

exceed 5°C during this addition. The solution was stirred at room temperature for one hour and poured into 100 g of ice. The organic layer was extracted with 250 ml of CH_2Cl_2 which was then dried over magnesium sulphate. Evaporation of the CH_2Cl_2 gave 8.1 g of N-nitro-pyrrolidine as a light yellow solid. Two recrystallizations from hot heptane gave 7.6 g (32%) of shiny white needles with a melting point of 56°C. Coburn and Ungnade reported a melting point of 58-59°C.

5. 2-Pyrrolidone

This preparation was adapted from that of Spath and Lintner [19].

The pressure chamber of the Parr Hydrogenator was cooled with liquid nitrogen until liquid NH_3 would remain in the chamber without evaporation. 80 ml of liquid NH_3 and 100 ml of γ -butyrolactone were then added to the chamber and it was sealed. When the chamber had risen to room temperature as evidenced by the disappearance of frost from the outside surface, it was wiped dry externally and placed in the heating chamber of the hydrogenator. The temperature of the hydrogenator was then raised to 200°C. The temperature in the hydrogenator was maintained between 183°C and 217°C for 2 hours during which period the pressure varied between 2250 psig and 1700' psig. At the end of this period, the hydrogenator was cooled to 100°C, at which time the excess NH_3 was vented. When the hydrogenator had cooled to 50°C, the pressure chamber was removed and the contents distilled at reduced pressure.

The 2-pyrrolidone was collected at 83-87°C at a pressure of 3 Torr. Any γ -butyrolactone which had codistilled was removed by freezing out the pyrrolidone at -5°C and pouring off the lactone. The identity of the lactam was established by ir and nmr spectra. The ir spectrum showed bands at 3300 cm^{-1} , 2900 cm^{-1} , 1625 cm^{-1} , and 1275 cm^{-1} . The nmr spectrum peaks are listed in section E.3 of the Results. The final yield was 42 g (41%) of 2-pyrrolidone.

6. N-Hydroxypyrrolidine

This preparation was adapted from that of Ruppert [20].

15 ml of ethyl formate and 60 ml of 30% H_2O_2 were added slowly to 20 ml of pyrrolidine in a 150 ml flask; stirred, and cooled in an ice-water bath. The temperature reached 90°C during addition.

The reaction mixture was extracted with CH_2Cl_2 . The solvent was extracted from the organic layer and the remaining viscous liquid was distilled in vacuo and the product collected at 70-75°C at 3 Torr.

The product was a colorless liquid which quickly yellowed on contact with the air. The final yield was 15 g (18%). Identity of the product was checked by nmr and ir spectra. The nmr spectrum peaks are listed in section E.1 of the Results. The ir spectrum showed peaks at 3400 cm^{-1} , 2900 cm^{-1} , and 1615 cm^{-1} .

7. Succinic Anhydride

150 g of succinic acid, 50 ml of acetic acid, and 150 ml of acetic anhydride were refluxed for 16 hours in a round bottom flask fitted

with a refluxing condenser. The solution was cooled and the liquid poured off. The solid product was washed several times with anhydrous ether then dried in a vacuum desiccator at 100 μ pressure. The yield was 107 g (84%) of shiny white needles which melted at 119°C.

8. N-Hydroxysuccinimide

This preparation was adapted from that of Anderson, Zimmerman, and Callahan [21].

50 g of carefully dried succinic anhydride and 35 g of dried hydroxylamine hydrochloride were combined in a 500 ml round-bottom flask on a rotary evaporator. The flask was rapidly heated to 135°C on an oil bath, volatile components being removed under vacuum from aspirator and caught in an ice-water cooled condenser and dry ice trap. Fusion occurred with the evolution of gases and an amber liquid formed during the next hour as the temperature was slowly raised to 160°C. Heating was then discontinued. When the temperature had dropped to 125°, the liquid was poured into 200 ml of rapidly stirred anhydrous ether. After the product had solidified, the ether was decanted and the residue heated to boiling with 200 ml of dry n-butanol. The mixture was filtered and the filtrate rapidly chilled to 0°C. After one hour, the crystalline product was collected by filtration and washed with n-butanol and ether. The crude product was recrystallized twice from hot ethyl acetate. The final product was a white crystalline solid which melted at 99°C. The yield was 10 g (18%). Anderson et al reported the same melting point.

9. Δ -1-Pyrroline - Oxide

This preparation was adapted from that of Bonnet [22] .

1.3 g of N-Hydroxypyrrolidine in 50 ml of chloroform were placed in a 250 ml Erlenmeyer flask fitted with a cork. 5 g of red mercuric oxide were added and the solution was stirred very rapidly for one hour and forty-five minutes. An additional 2 g of red mercuric oxide were added and stirring was continued for an additional two hours.

The solution was filtered and the solvent evaporated from the filtrate in a rotary evaporator. The residue, a viscous dark red-brown liquid was stored in the dark for 24 hours. After this time, the hydroxylamine was evaporated at 100 μ pressure and the infrared spectrum of the product, a waxy brown solid was obtained. The infrared spectrum was virtually identical to that obtained by Thesing and Sirrenberg [23] for the nitron, with peaks at 3400 cm^{-1} , 2900 cm^{-1} , 1615 cm^{-1} , and 1350 cm^{-1} . These authors obtained an ultraviolet spectrum with λ_{max} at 232 nm.

The waxy solid was dissolved in absolute methanol and the solvent was evaporated in the fume hood. A white solid was seen to form during evaporation of the solvent but it was not isolated.

Addition of acetone to the residue resulted in formation of some red-brown solid. The infrared spectrum of this solid was obtained. It contained peaks at the same wavelengths as the nitron.

B. ELECTRON SPIN RESONANCE STUDIES

1. Dinitropiperazine

a. In solution

A solution of dinitropiperazine 0.09 M in dimethylformamide was placed in a flow apparatus in the Electron Paramagnetic Resonance Spectrometer. Nitrogen gas was bubbled through the system to purge it of any entrapped air. The cavity of the spectrometer was irradiated with a Christie 200 watt ultraviolet radiation source. The solution was flowed at various speeds through the cavity and the electron spin resonance spectra were recorded. It was found that flowing or not flowing the solution had very little effect. After the solution had been removed from the spectrometer a sample of pure dimethylformamide was irradiated with the same source to confirm that it was the nitramine and not the solvent which gave the esr signal. This esr spectrum and those of other compounds mentioned here are shown in the Results.

b. A 4mm quartz esr tube was filled to a depth of about $1\frac{1}{2}$ inches with dinitropiperazine. This tube was irradiated for 10 minutes with a 200 watt ultraviolet radiation source. The tube was then placed in the cavity of the esr spectrometer. The esr signal of the solid powder was obtained.

2. RDX

In a similar manner to that for dinitropiperazine, a solid sample of RDX was photolyzed for 45 minutes and the esr signal of the solid powder was obtained.

3. HMX

A sample of solid HMX was photolyzed under conditions identical to those used for RDX and for the same period, and the esr signal was obtained.

4. N-Nitropyrrolidine

A solution of nitropyrrolidine in PDCC was photolyzed in a 0.5 mm flat cell in the cavity of the esr spectrometer. The solution esr signal was obtained.

5. N-Hydroxysuccinimide

A solution of N-Hydroxysuccinimide, 100 mg in 10 ml of DPCC was photolyzed in a 0.5 mm flat cell in the cavity of the esr spectrometer. A weak esr signal of the solution was obtained.

C. MASS SPECTRAL STUDIES

All of the mass spectra were obtained in the CEC Type 21-103 Mass Spectrometer.

1. Dinitropiperazine

a. Photolysis with no filter

A sample of approximately 100 mg was dissolved in sufficient acetonitrile to make a saturated solution. The solution was placed in a solution combined 10 cm uv - ir gas cell. The solvent was evaporated under reduced pressure and the dinitropiperazine deposited in a thin layer on the quartz window. The cell was evacuated at 20 μ pressure for 12 hours. The cell was irradiated for 24 hours with an Oriel 200 watt ultraviolet radiation source. The uv source was shut

down and the volatile photolysis products collected in a 200 ml gas cell which had been evacuated to 20 μ . The contents of this cell were examined in the mass spectrometer at ionizing voltages of 20 v and 70 v.

b. Photolysis with 270 nm filter

The procedure used was similar to that above except that the uv source was a Christie 200 watt uv source and a 270 nm filter was placed between the source and the cell in an effort to minimize interaction between N₂O gas and other products. The ionizing voltages used in this case were 16 V and 70 V.

2. N-Nitropyrrolidine

a. Photolysis with no filter

A similar procedure to that used for dinitropiperazine was used for nitropyrrolidine. In this case the photolysis was carried out on the sample deposited on the uv window of a combined uv/ir gas cell. The pressure to which the sample was evacuated was 50 μ , the vapour pressure of nitropyrrolidine at 15°C. The Oriel uv source was used in this case.

b. Photolysis with 270 nm filter

In this instance, the sample was deposited on a quartz window of a cell equipped with a water jacket to keep the reaction temperature constant at 15°C. A 270 nm filter was fitted over the quartz window to minimize reactions of the N₂O gas. This procedure was repeated on another occasion but the 270 nm filter was suspected of no longer being effective.

- c. Attempt at low temperature fractionation of gaseous products

A sample of nitropyrrolidine was deposited from CH_2Cl_2 on the uv window of the combined uv/ir gas cell. The cell was pumped down to $100\ \mu$ pressure after having been evacuated at 100 Torr for 12 hours. It was shown from the mass spectra that this procedure resulted in some CH_2Cl_2 remaining which contaminated the photolysis products. After 24 hour photolysis using the 270 nm filter, the cell was placed on the vacuum system and placed in parallel at a system pressure of less than one with a 200 ml gas cell cooled to -100°C with an ethanol-liquid nitrogen slurry. After one-half hour, a liquid nitrogen trap was placed under the combined uv/ir cell and the system allowed to equilibrate for 5 minutes after which the cells were isolated. Mass spectra were obtained of both gaseous mixtures.

3. N-Nitropiperidine

a. Two ml of N-nitropiperidine were placed in a quartz walled cell and evacuated to $50\ \mu$ pressure at -198°C . The cell was then irradiated with the Christie 200 watt uv source for 24 hours and the gaseous products collected in a 200 ml gas cell which had been evacuated to $20\ \mu$. The gases were examined in the mass spectrometer at an ionizing voltage of 70 V.

b. Photolysis with 270 nm filter

Two ml of N-nitropiperidine were evacuated to $500\ \mu$ pressure in the water cooled cell. This procedure did not successfully

remove all the air from the system. After 24 hours photolysis with the Christie uv source and the 270 nm filter which was only partially effective due to heavy use, the gaseous products were collected in a 200 ml gas cell. The gaseous products were examined in the mass spectrometer at ionizing voltages of 16 V and 70 V.

4. 4-Methyl-1-Nitropiperidine

Two ml of 4-methyl-nitropiperidine were evacuated until boiling commenced (500 μ pressure) in the water cooled cell. Photolysis was carried out for 24 hours using the Christie 200 watt uv source and the partially effective 270 nm filter. The gaseous products were collected in a 200 ml gas cell and examined in the mass spectrometer at ionizing voltages of 16 V and 70 V.

5. N-Hydroxypyrrolidine/N₂O

Two ml of N-hydroxypyrrolidine were placed in the water cooled cell. The cell was then evacuated to a pressure of 1 Torr. N₂O gas was introduced into the cell in such a manner as to minimize contact with air. The N₂O gas and the hydroxylamine were allowed to equilibrate for one-half hour. The mixture was photolyzed for 24 hours using the Christie uv source. At the end of this period, the gaseous products were collected in a 50 ml gas cell and examined in the mass spectrometer.

D. KINETIC STUDIES OF PHOTOLYSIS OF NITROPYRROLIDINE

1. Nitropyrrolidine in n-heptane

A solution of nitropyrrolidine 2.5×10^{-4} M in n-heptane (spectral grade) was photolyzed in a uv cuvette. The uv spectrum of the sample as compared with that of a sample of n-heptane (reference) was recorded at the following photolysis intervals (minutes): 0.0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0, 30.0, 40.0.

Photolysis was carried out with the Oriel uv source. No filter was used.

2. Nitropyrrolidine/Acrylonitrile

A solution of nitropyrrolidine 0.864 M in acrylonitrile was prepared. One μ l of this solution was added to 25 ml n-heptane. Photolysis was carried out in a similar manner to that given above. In this instance the sample uv spectrum was obtained at periods of (minutes): 0.0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 200.

Nitramine concentration at the beginning of this study was 3.96×10^{-5} M.

E. ATTEMPTED ADDUCT FORMATION

1. Photo-adduct of Photolysis Products of N-Nitropyrrolidine and Acrylonitrile

a. Photolysis in the absence of a filter

A solution of N-Nitropyrrolidine 0.864 M in acrylonitrile was prepared and photolyzed. The appearance and ir

spectrum of the solution were examined at the intervals given in Table II.

TABLE II

Appearance of Solution during Photolysis: N-Nitropyrrolidine in Acrylonitrile.

Photolysis Period (hours)	Appearance
0	Very pale yellow liquid
1	Deep yellow liquid
4	Yellow-orange liquid
8	Orange-brown liquid containing a small amount of dark solid.
24	Red-brown liquid containing a large amount of dark solid.
45	Very dark brown oily solution.

An attempt was made to isolate the products by column chromatography but only a red-yellow oil, an unknown solid product, and starting material could be isolated. The products were also examined at the same intervals by gas chromatography. The liquid and residue remaining on completion were examined in the same manner.

b. Photolysis with a 230 nm filter

A solution of 0.747 g of nitropyrrolidine in 0.5 ml of acrylonitrile was placed in a 4mm esr tube for photolysis. This gave a 14% excess of acrylonitrile. The solution was photolyzed and examined

in the Hitachi-Perkin Elmer Model R20A Nuclear Magnetic Resonance Spectrometer at intervals of photolysis to 24 hours. This was accomplished by placing the 4mm esr tube inside a 5mm nmr tube. After photolysis, an attempt was made to separate the photolysis products but again only starting material, an unknown white crystalline solid, and a red-brown oil were recovered.

c. Photolysis in a 50/50 dioxane:acrylonitrile
solution using a 290 nm filter

290.5 mg of nitropyrrolidine was dissolved in 5 ml of dioxane and 5 ml of acrylonitrile. The solution was placed in the water-jacketed cell and photolyzed for 50 hours using the Christie uv radiation source and a 290 nm filter.

At the end of the photolysis period, there remained a cream-colored solid (187 mg) and approximately 8 ml of a yellow liquid.

The solid did not melt below 200°C and slowly turned brown on heating. Some areas turned a dark red-brown upon heating, indicating a heterogeneous system. Treating the solid with hot heptane and then washing the remainder with CHCl_3 resulted in a recovery of starting material and a red-brown oil plus a gray-white solid. No adduct was found. Distillation of 5 ml of the liquid phase resulted in recovery of a solid which recrystallized from hot heptane and in the ir resembled nitropyrrolidine except for a peak at 2200 cm^{-1} indicating some nitrile present. The nmr spectrum obtained from this product was that of nitropyrrolidine. It was thus assumed that no adduct had formed.

2. Dark Phase Adduct of Photolysed Dinitropiperazine and Acrylonitrile

0.500 g of dinitropiperazine was photolysed in a uv cuvette for 24 hours with the Christie uv radiation source and a 270 nm filter. After photolysis, the solid was dissolved in 10 ml of acrylonitrile and stored in the dark for 30 days.

The product (50 mg), which was soluble in acetone, was dissolved in d-6 acetone and the nmr spectrum obtained. This indicated a complex series of peaks belonging in all probability to several products. An attempt was made to separate the yellow, semi-solid products by column chromatography.

A 10 mm column was made up of activity one alumina in 5/1 ethyl acetate-chloroform. The products which were soluble in 5/1 Et-oAc/CHCl₃ were added to the column in this solution and the column was eluted with 8 ml of 5/1 EtoAc/CHCl₃. The products soluble in ethanol and acetonitrile were then added to the column in their respective solvents. The column was then eluted with the following solvents:

- 10 ml of EtoAc-CHCl₃ (5/1)
- 16 ml of chloroform
- 16 ml of ethanol
- 16 ml of acetone
- 16 ml of acetonitrile
- 16 ml of acetone
- 16 ml of 3/1 acetone - water

16 ml of 1/1 acetone - water

16 ml of 1/3 acetone - water

16 ml of water.

None of these elutions resulted in recovery of any material other than a white solid whose infrared spectrum very closely resembled that of dinitropiperazine.

3. Dark Phase Adduct of Photolyzed N-Nitropyrrolidine and Acrylonitrile

361 mg of nitropyrrolidine were photolyzed in the water-jacketed cell for 25 hours 30 minutes using the Christie uv source and no filter. The products of photolysis were then dissolved in 10 ml of acrylonitrile and stored in the dark for 47 hours.

At this time, the solvent was evaporated and the products examined. A yellow solid remained which gave the same nmr spectrum as nitropyrrolidine in deuteriochloroform. The product was recrystallized from hot heptane. 134.5 mg of nitropyrrolidine were recovered from hot heptane. A red-yellow oil which was insoluble in heptane was recovered. This product was shown by the ir spectrum to be the same red-yellow oil recovered from all previous attempts to form a nitropyrrolidine-acrylonitrile adduct. The ir spectrum showed no evidence of a nitrile peak, but showed peaks at 3300 cm^{-1} , 2900 cm^{-1} , 1615 cm^{-1} , and 1450 cm^{-1} .

F. NUCLEAR MAGNETIC RESONANCE SPECTROMETRY STUDIES
OF SUSPECTED INTERMEDIATES

1. N-Hydroxypyrrolidine

2.0 ml of n-hydroxypyrrolidine were photolyzed in the water-jacketed cell for 16 hours. The sample was then decanted and a portion of it examined for changes of the nmr spectrum. The nmr spectrum of this and the other studies mentioned here are included in the Results.

2. N-Hydroxypyrrolidine/N0

The liquid products from mass spectral study were examined for changes in the nmr spectrum. The products were then distilled to remove starting material and the ir spectra of the oily residue was examined for similarities to the products of photolysis of nitropyrrolidine.

3. 2-Pyrrolidone

2.0 ml of 2-pyrrolidone were photolyzed for 24 hours in the water-jacketed cell. The nmr spectrum of the products was then examined for changes.

G. GASEOUS INFRA-RED ABSORPTION STUDY

The gaseous products from the photolysis of dinitropiperazine in the absence of any filter were examined spectrophotometrically in the infra-red region before being used for mass spectral determinations. The infra-red spectrum of the gases was obtained on the Perkin-Elmer 337 Spectrophotometer.

H. THERMAL SENSITIVITY OF N,N-DINITROPIPERAZINE

The samples listed below were placed in an oven for one hour in an effort to determine the effect of high temperatures on N,N-dinitropiperazine. The infra-red and nuclear magnetic resonance spectra were then obtained in an effort to determine whether or not any chemical decomposition had occurred.

Sample 1.

Oven temperature: 150°C

Weight loss: $0.784 - 0.0723 = 0.0061$ gm.

% weight loss = 7.8%

Sample 2.

Oven temperature: 180°C

Weight loss: $0.0973 - 0.0527 = 0.0446$ gm.

% weight loss = 45.8%

Sample 3.

Oven temperature: 200°C

Weight loss: $0.0903 - 0.0110 = 0.793$ gm.

% weight loss = 87.8%

I. IMPACT SENSITIVITY

The impact sensitivity of N,N-dinitropiperazine was obtained with the aid of Mr. R.S. Watkins on the Impact Sensitivity apparatus described in reference [24]. The point for 50% detonation probability obtained in this manner was 115 cm.

J. PHOTOLYSIS SOLID PRODUCT IDENTIFICATION

The non-gaseous final products of the photolysis of solid N-nitropyrrolidine or of the nitramine in solution appear to have been the same. These were a yellow oil or oils and a white crystalline solid which may have been a mixture of several products and was called X. The same product, X, was obtained from the photolysis of N,N-dinitropiperazine and by Mr. Bodnar [25] from the photolysis of N-nitropiperidine.

Solubility tests on X were carried out. It was soluble in ethanol, concentrated HCl, water, dimethylformamide, and hot acetonitrile. X was insoluble in methanol, acetone, ether, hexane, and concentrated NaOH.

A sodium fusion test was carried out with negative results. This would indicate that either X does not contain nitrogen or that any nitrogen was lost as gaseous products in the fusion. X does not give a positive nitramine test or a positive nitro group test.

An attempt was made to determine the structure of X from the nuclear magnetic resonance spectrum. The test was a failure. A solution of 30 mg per ml had been attempted but this proved to be above the saturation limit for X in D₂O. Addition of deuterioacetic acid allowed complete solvation but no nmr signal was detected. The only visible change was the increase in the size of the acidic proton peak of the deuterioacetic acid indicating hydrogen exchange with X. Similar results in D₂O were obtained with N-hydroxysuccinimide. The ultraviolet spectrum of X in ethanol indicated no uv absorption above 220 nm.

The infra-red absorption spectrum was very complex. The ir spectrum is included in the Results section of this report as Figure 9. On the basis of the sodium fusion test and the solubility of X, it was included in the solubility class S_2 [26] . This indicates the possibility of a polyol, simple sugar or carbohydrate. A Schiff test carried out on X was negative. Treatment of X with periodate before the Schiff's test gave the same results.

Melting point data obtained on X indicated that either it was a mixture of compounds or a compound with no definite melting point. It softens slightly at 185°C , undergoes partial decomposition at 195°C , turning a red-brown color at that time, but does not completely melt below 300°C .

Mr. Bodnar obtained a positive Tollen's reagent test on the yellow oil which is produced from the photolysis of N-nitropyrrolidine. A similar test run on X was negative.

IV. RESULTS

A. ELECTRON SPIN RESONANCE STUDIES

When N,N-dinitropiperazine 0.09 M in dimethylformamide was photolyzed, an esr signal was seen. This was the first concrete evidence of a radical mechanism for the photochemical decomposition of N,N-dinitropiperazine. Professor Tolles, an Electron Spin Resonance Spectroscopist, stated that the spectrum was probably that of a nitroxide. This was later proven correct by Mr. Bodnar [25]. The esr signal (Figure 1) obtained in solution had a half-life of 6 seconds. Photolysis of the solvent alone confirmed that the esr signal was from the nitramine and not from the solvent.

Photolysis of the solid powder N,N-dinitropiperazine was carried out at a location remote from the spectrometer and the photolyzed sample was then transported to the esr spectrometer. The signal obtained (Figure 2) was confirmed by Mr. Bodnar [25] by single crystal studies to be the nitroxide. The esr signal showed no visible attenuation one-half hour after the photolysis had ceased and a weak signal was detectable two days later.

Photolysis of RDX in the solid powder form, carried out in the same manner as for N,N-dinitropiperazine, gave an esr signal (Figure 3). This also was identified by Mr. Bodnar [25] as the nitroxide on the basis of single crystal studies. The photolysis of HMX produced a much weaker

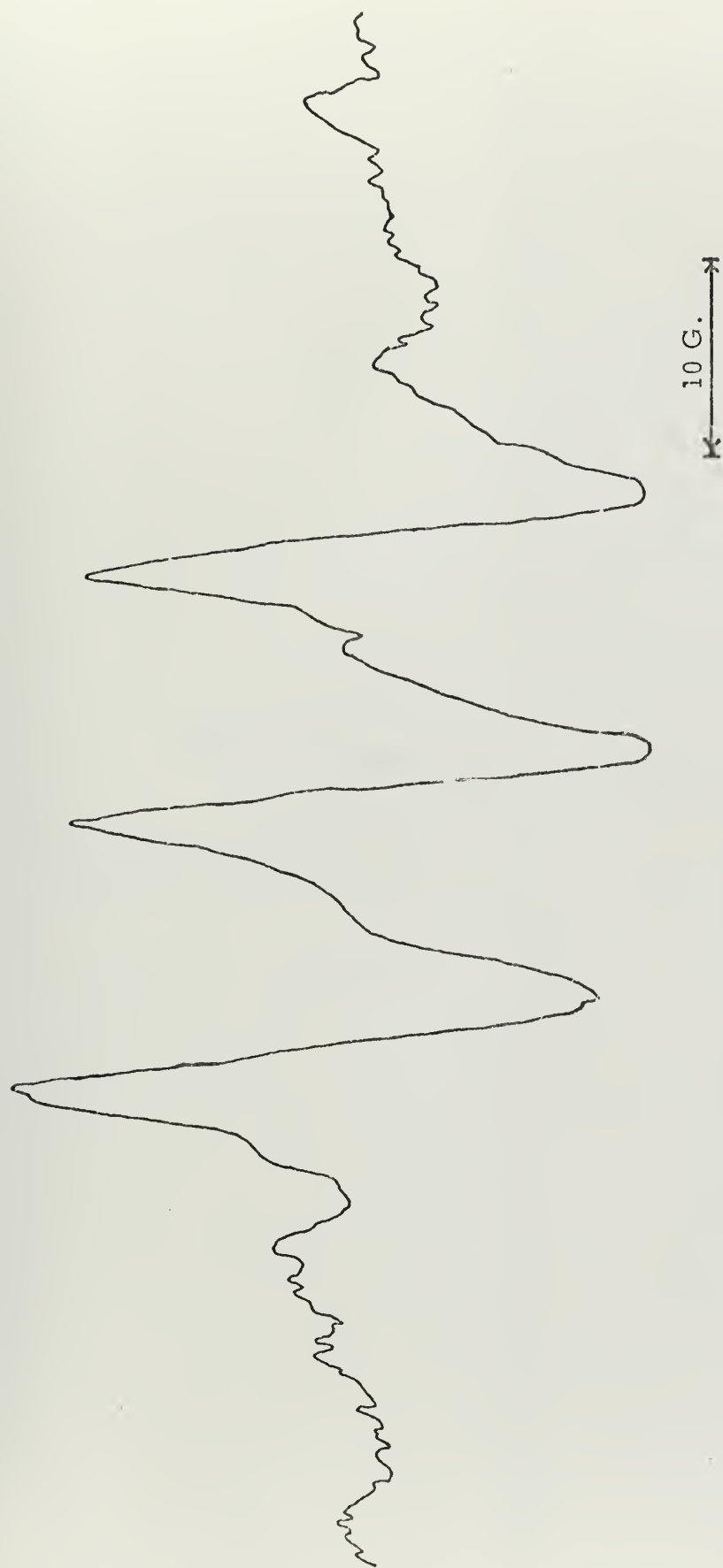


FIGURE 1.

ELECTRON SPIN RESONANCE SIGNAL FROM
PHOTOLYSIS OF N,N-DINITROPHENAZINE IN DIMETHYLFORMAMIDE

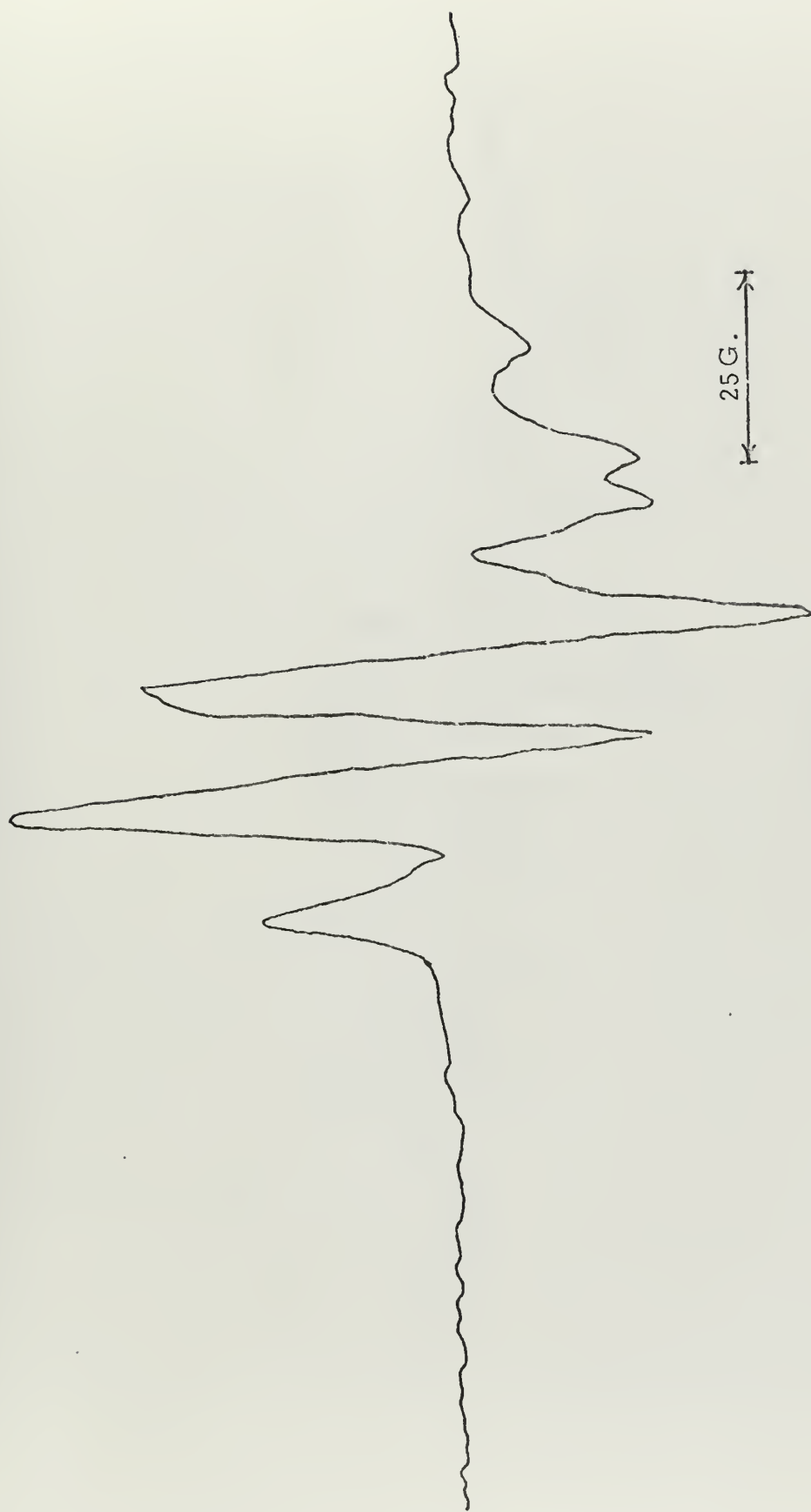


FIGURE 2.
ELECTRON SPIN RESONANCE SIGNAL FROM PHOTOLYSIS
OF N,N-DINITROPIPERAZINE SOLID POWDER

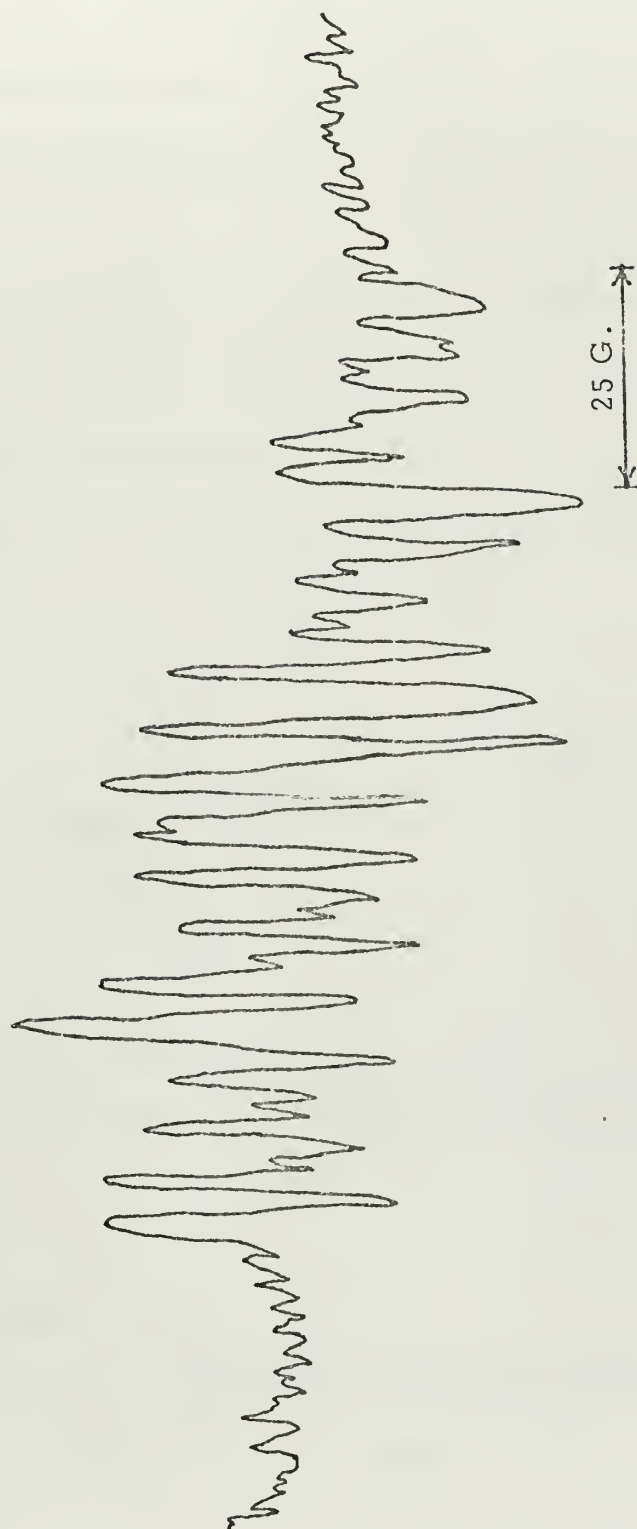
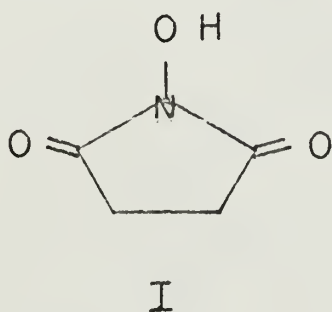


FIGURE 3.

ELECTRON SPIN RESONANCE SIGNAL FROM PHOTOLYSIS OF RDX SOLID POWDER

esr signal (Figure 4). The signal appeared, however, to be identical to that obtained from RDX. This would seem to indicate that the same or a very similar nitroxide was formed in the photolysis of these two nitramines. No attempt was made to definitely classify the esr spectrum obtained in this case.

It was expected that photolysis of N-Hydroxysuccinimide (I) would give a simple 3-line spectrum. This proved to be the case. The spectrum was, however, very weak indicating that either the nitroxide had a very short half-life or that the molecule had a very weak absorption in the ultraviolet. The esr spectrum is shown in Figure 5.



The photolysis of N-nitropyrrolidine in solution also yielded a nitroxide intermediate visible in the Electron Spin Resonance Spectrometer (Figure 6).

B. MASS SPECTRAL STUDIES

The first attempts at photolysis of N,N-dinitropiperazine used a similar procedure as had been used by Torbit, J.B. [8]. The photolyses were carried out with the nitramine deposited on the quartz window of the

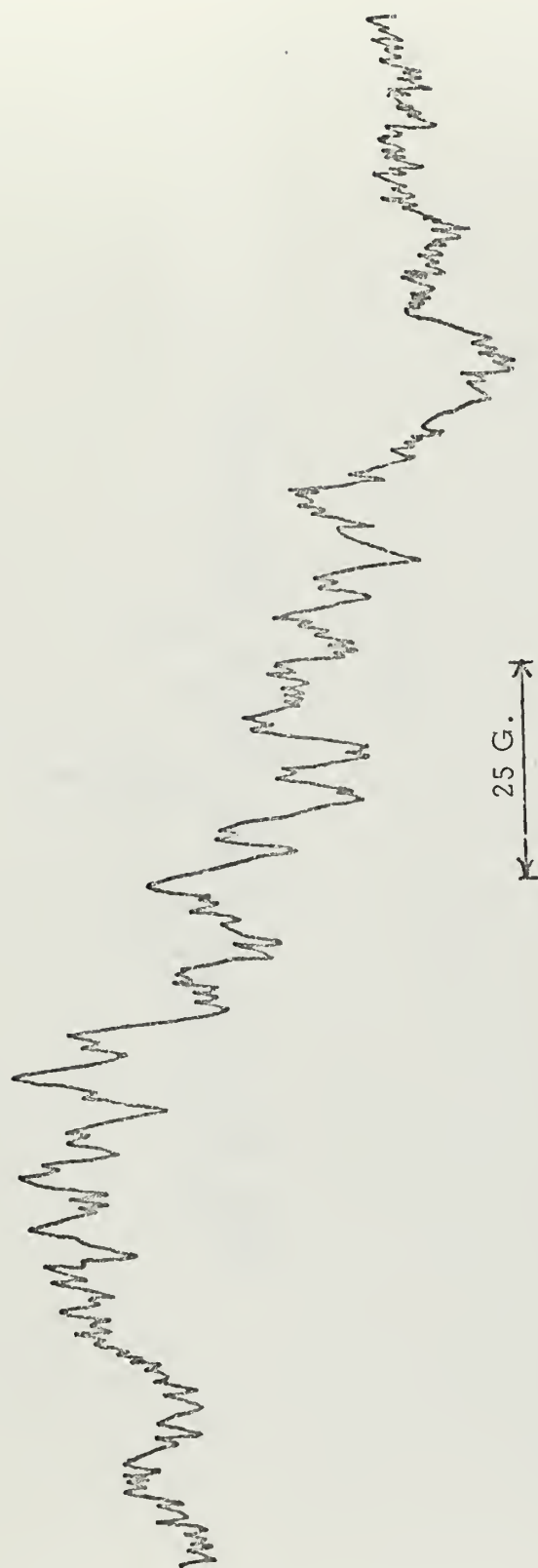


FIGURE 4.

ELECTRON SPIN RESONANCE SIGNAL FROM PHOTOLYSIS OF HMX SOLID POWDER



FIGURE 5.

ELECTRON SPIN RESONANCE SIGNAL FROM PHOTOLYSIS OF
N-HYDROXYSUCCINIMIDE IN DPCC.

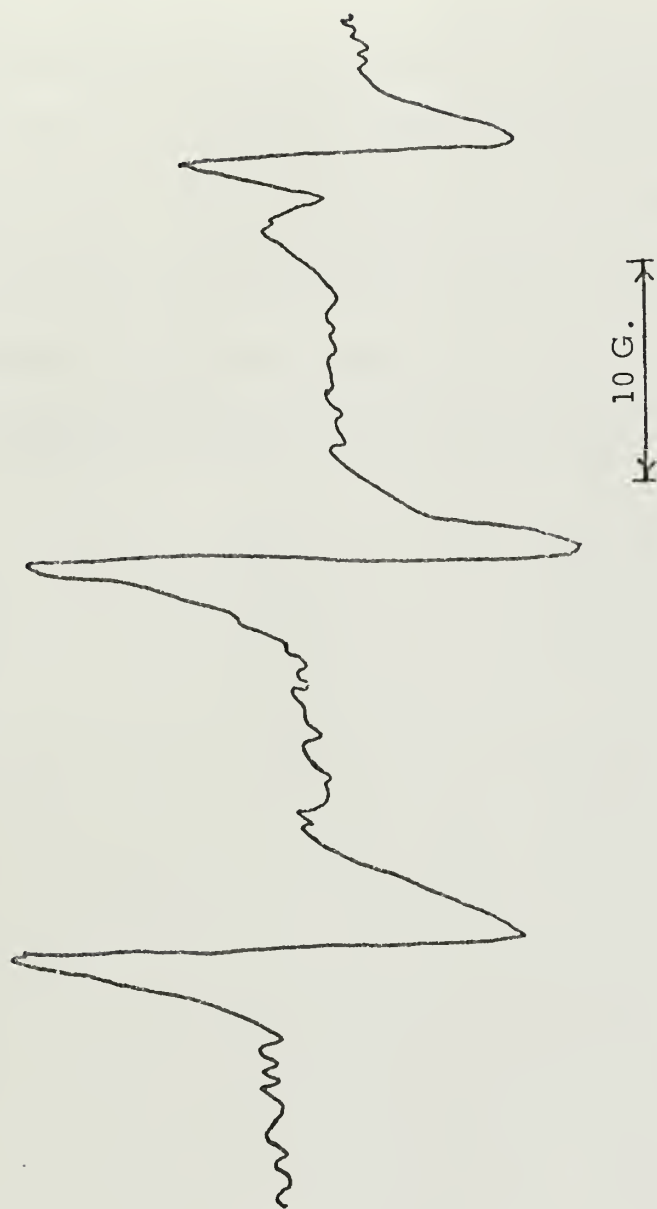


FIGURE 6 .
ELECTRON SPIN RESONANCE SIGNAL FROM PHOTOLYSIS OF
N-NITROPYRROLIDINE IN DPCC .

combined uv/ir gas cell. Upon discovery of the nitroxide mechanism, it was considered surprising that there were almost as intense peaks at M/E 28 as at M/E 30.

Since this was believed to be due to photochemical smog reactions, it was decided to use a filter in other photolyses to minimize these reactions. The 270 nm filter was chosen since this wavelength corresponded to a low point in the uv absorption spectrum of nitric oxide gas [27]. The differences in the mass spectra which followed are readily apparent from comparison of columns 1 and 3, and 2 and 4, of Table III.

TABLE III

Mass Spectra of Gaseous Products (at very Low Pressures) of Photolysis
of N,N-Dinitropiperazine

Ionizing Voltage Filter used M/E	PEAK INTENSITY			
	20 V	70 V	16 V	70 V
	None	None	270 nm	270 nm
	1	2	3	4
12	10.5	7.5	Not Recorded	Not Recorded
13	2.5	1.5		
14	66.5	32.5		
15	4	3		
16	19	11		
17	6	3.5		
18	28	9.5	0.5 2 11.5 2 100 3.5 - - - - -	4.5 9.5 24.5 3.5 100 5 1 7 1.5 4.5 3
25	-	1		
26	5.5	3		
27	13.5	8		
28	65	37		
29	8.5	4		
30	<u>100</u>	<u>100</u>		
31	4	2		
32	3	2		
35	-	-		
36	-	-		
37	-	-		
38	4	3		

TABLE III (continued)

Ionizing Voltage Filter used M/E	PEAK INTENSITY			
	20 V	70 V	16 V	70 V
	None	None	270 nm	270 nm
	1	2	3	4
39	10	4.5	0.5	11
40	19	11.5	0.5	5.5
41	41	22	7.5	19
42	6	2.5	3.5	16.5
43	7.5	3.5	5.5	22
44	70	60	4	21
45	2	2	0.5	2
46	1	1	-	1
47	-	-	1.5	19
48	-	-	0.5	9
49	3	0.5	0.5	6.5
50	-	-	-	3
51	1	1	-	1
53	1	1	-	1
54	1	1	-	1
55	-	-	-	1
56	9	4	-	1
57	8.5	3.5	2	3.5
58	-	0.5	0.5	1.5
68	-	-	1	6
69	2	1	3	13.5
70	-	-	1.5	9.5
71	-	-	1.5	6.5

TABLE III (continued)

	PEAK INTENSITY			
Ionizing Voltage	20 V	70 V	16 V	70 V
Filter used	None	None	270 nm	270 nm
M/E	1	2	3	4
72	-	-	-	1
79	-	1	-	-
81	-	0.5	-	-
83	-	-	7.5	-
85	7.5	2	4.5	-
86	-	-	0.25	-
87	1	1	0.5	-
117	-	-	-	1
118	-	-	-	1
119	-	-	-	1
120	-	-	-	1

An even greater disparity between the predicted and experimental peak ratios for M/E 28 and 30 occurred in the case of the photolysis of N-nitropyrrolidine. This changed markedly with the use of the 270 nm filter to limit the effects of NO. Comparison of columns 2 and 3 of Table IV shows the effect of the use of a filter on the photolysis products' mass spectra.

TABLE IV

Mass Spectra of Very Low Pressure Gaseous Photolysis Products of
N-Nitropyrrolidine

Ionizing Voltage Filter M/E	PEAK INTENSITY		
	20 V	70 V	70 V
	None	None	270 nm
	1	2	3
12	-	2	1
13	-	0.25	0.5
14	8.5	27	-
15	2	2	1.5
16	3	7	3
17	-	0.25	0.5
18	-	-	1
25	-	-	0.5
26	-	2	1
27	2	3.5	4.5
28	<u>100</u>	<u>100</u>	13
29	2	3.5	5.5
30	21	32	<u>100</u>
31	-	0.5	0.5
32	16.5	4.5	0.25
38	-	1.5	1
39	-	2.5	3.5
40	1.5	8	4
41	5	8.5	14
42	-	1.5	4.5

TABLE IV (continued)

Ionizing Voltage Filter M/E	PEAK INTENSITY		
	20 V	70 V	70 V
	None	None	270 nm
	1	2	3
43	3	5.5	10
44	6.5	8	13
45	-	0.25	0.25
46	-	0.25	-
47	-	-	0.25
49	-	-	1
50	-	-	0.25
51	-	-	1
52	-	-	0.25
53	-	-	0.25
55	-	0.25	1.5
56	-	1	5.5
57	-	2	4
58	-	0.5	1
59	2	2	-
69	-	-	0.5
70	-	-	0.5
71	-	-	1.5
78	-	-	1
84	-	-	1
85	-	-	1
86	2.5	1	1.5

TABLE IV (continued)

Ionizing Voltage Filter M/E	PEAK INTENSITY		
	20 V	70 V	70 V
	None	None	270 nm
	1	2	3
87	-	-	0.25
98	-	-	0.25
99	-	-	0.25
142	-	-	0.25

The attempt to carry out a low temperature fractionation on the photolysis products of N-nitropyrrolidine was marred by the presence of some CH_2Cl_2 in the reaction mixture. This was present from the solvent. When the data was analyzed, the peaks known to be due to CH_2Cl_2 were omitted. The remaining peaks, all thought to be representative of the photolysis products are tabulated in Table V. No peaks below M/E 23 were recorded because of the mass range scales used on the spectrometer.

TABLE V

Mass Spectra of Very Low Pressure Gaseous Products of Photolysis of
N-Nitropyrrolidine. Low Temperature Fractionation Attempted.

Ionizing Voltage Collection T°C M/E	PEAK INTENSITY			
	16 V	70 V	16 V	70 V
	-198	-198	-100	-100
	1	2	3	4
23	-	-	-	0.5
24	-	-	-	0.25
26	0.5	0.5	1.5	6
27	1.5	2	21	51
28	10	11.5	41	44
29	3.5	2	43	52.5
30	<u>100</u>	<u>100</u>	<u>100</u>	79
31	1	0.5	12	8.5
32	1	0.5	-	0.5
38	-	0.25	-	5
39	-	1	2	33.5
40	-	0.5	2	7
41	1	2	37	74.5
42	1	0.5	31	37
43	4.5	4	92	<u>100</u>
44	8.5	29.5	16.5	13.5
45	-	0.5	4	6
46	-	-	1.5	1
47	-	1.5	9.5	47.5
48	-	0.5	11.5	21.5

TABLE V (continued)

Ionizing Voltage Collection T C M/E	PEAK INTENSITY			
	16 V	70 V	16 V	70 V
	-198	-198	-100	-100
	1	2	3	4
49	3.5	2	65	74.5
50	-	1	6	13.5
51	3.5	2	64	70.5
52	-	0.25	0.5	7
53	-	0.25	-	6
54	-	-	0.25	13.5
55	-	0.5	6	7
56	1.5	1	55.5	52.5
57	4	3	6	86.5
58	-	-	-	5
68	-	-	-	1
69	-	0.5	4.5	7
70	-	-	4.5	7
73	-	-	11.5	13
74	-	-	0.5	2
75	-	-	-	1
76	-	-	-	1
77	-	0.5	-	12.5
78	-	0.5	8	14
79	-	0.5	0.25	6
80	-	-	-	1
81	-	-	-	0.25
82	-	-	-	5
83	0.5	1	8.5	16

TABLE V (continued)

Ionizing Voltage Collection T C M/E	PEAK INTENSITY			
	16 V	70 V	16 V	70 V
	-198	-198	-100	-100
	1	2	3	4
84	2	3	69	50
85	0.5	1	8.5	16.5
86	0.5	2	21.5	80
87	-	0.5	0.5	3.5
88	-	-	6.5	13
89	-	-	-	2
98	-	-	-	2
99	-	-	-	2
142	-	-	-	2.5
143	-	-	-	0.25

The mass spectral data for the photolysis of N-nitropiperidine are tabulated in Table VI. As was previously mentioned, although the 270 nm filter was used for 2 of the runs, it is not considered to have been effective. In column 2, no peaks below M/E 39 were measured due to the range scale in use.

TABLE VI

Mass Spectra of Very Low Pressure Gaseous Photolysis Products of
N-Nitropiperidine

Ionizing Voltage Filter M/E	PEAK INTENSITY		
	70 V	16 V	70 V
	None	270 nm	270 nm
	1	2	3
12	1	NOT MEASURED	-
14	32		64.5
15	2		2.5
16	6.5		9.5
17	-		1
18	-		2.5
26	-		1
27	0.25		2
28	32.5		<u>100</u>
29	1.5		5.5
30	<u>100</u>		4
31	1.5		-
32	0.5		86.5
39	0.25		2
40	0.25	4	1.5
41	0.5	5	1.5
42	0.5	5	1.5
43	1	<u>100</u>	15
44	30.5	4	12.5
55	1.5	-	0.5
56	1.5	7.5	1.5

TABLE VI (continued)

Ionizing Voltage Filter M/E	PEAK INTENSITY		
	70 V	16 V	70 V
	None	270 nm	270 nm
	1	2	3
57	1.5	5	0.5
58	1.5	27.5	4
69	0.5	-	0.5
70	2	-	-
71	8.5	-	-
81	-	-	0.5
82	-	-	1
83	1	-	0.5
84	1.5	5	-
85	6	-	-
98	1.5	-	-
99	1.5	-	-
111	0.5	-	-
112	1	-	-

The ratio of the peaks for M/E 28 and 30 for 4-methyl-nitropiperidine make it obvious that the filter used was no longer effective. The mass spectral data is tabulated in Table VII.

TABLE VII

Mass Spectra of Very Low Pressure Gaseous Photolysis Products of
4-Methyl-N-Nitropiperidine

Ionizing Voltage M/E	PEAK INTENSITY	
	16 V	70 V
	1	2
12		2.5
13		5.5
14		19.5
15		<u>100</u>
16		4
17		10
18		11.5
19		1.5
20	NOT MEASURED	1.5
25		3.5
26		15
27		23
28		30
29		12.5
30		3
31		16.5
32		5.5
36		1.5
37		6
38		7.5
39	6	14.5
40	2	3

TABLE VII (continued)

Ionizing Voltage M/E	PEAK INTENSITY	
	16 V	70 V
	1	2
41	3	10
42	19.5	22.5
43	<u>100</u>	95
44	8.5	10
45	5	5
46	1.5	11
47	-	0.5
48	-	0.25
49	-	0.25
50	-	0.25
51	-	0.25
52	-	0.5
53	-	1.0
54	-	0.5
55	1.5	2.5
56	5	5
57	1.5	2.5
58	77	65.5
59	2	2.5
60	-	0.25
69	1	1
83	0.5	0.5
84	3.5	4
85	0.25	0.5

The mass spectral data for the photolysis of N-Hydroxypyrrolidine in the presence of N₂O is given in Table VIII. Ionizing voltage was 70 V.

TABLE VIII

Mass Spectrum of Very Low Pressure Gaseous Products of Photolysis of N-Hydroxypyrrolidine in the Presence of N₂O.

M/E	PEAK INTENSITY
13	0.25
14	5
16	8.5
18	0.5
25	0.5
26	2.0
27	2.0
28	<u>100</u>
29	3
30	8.5
44	8.5

C. KINETIC STUDIES

The change of the ultraviolet spectrum of N-nitropyrrolidine in n-heptane as photolysis progressed is shown in Figures 7 and 8.

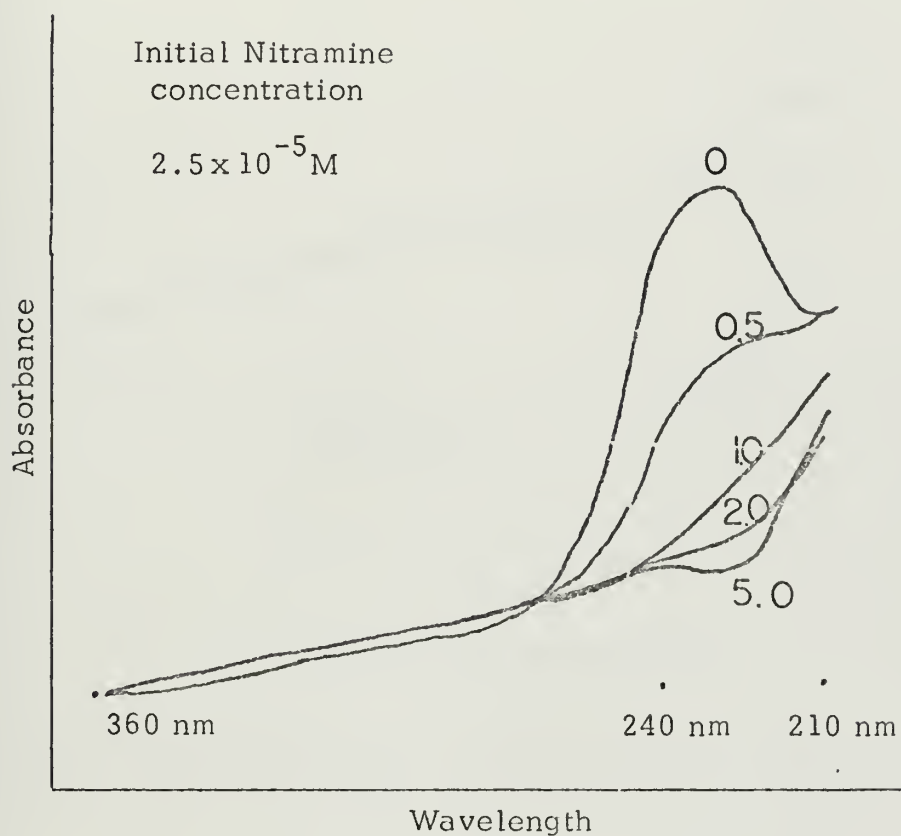


FIGURE 7.
ULTRAVIOLET ABSORBENCE
vs.
PHOTOLYSIS TIME (MIN.)
FOR N-NITROPYRROLIDINE IN N-HEPTANE

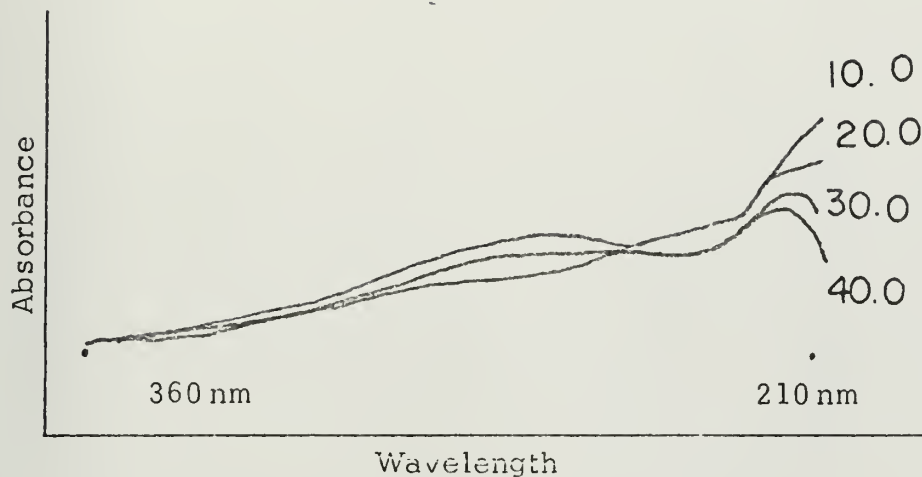


FIGURE 8.

ULTRAVIOLET ABSORBENCE

vs.

PHOTOLYSIS TIME (MIN.) FOR N-NITROPYRROLIDINE IN N-HEPTANE

The change in the ultraviolet spectrum of N-nitropyrrolidine and acrylonitrile in n-heptane with photolysis time is shown in Figures 9 and 10.

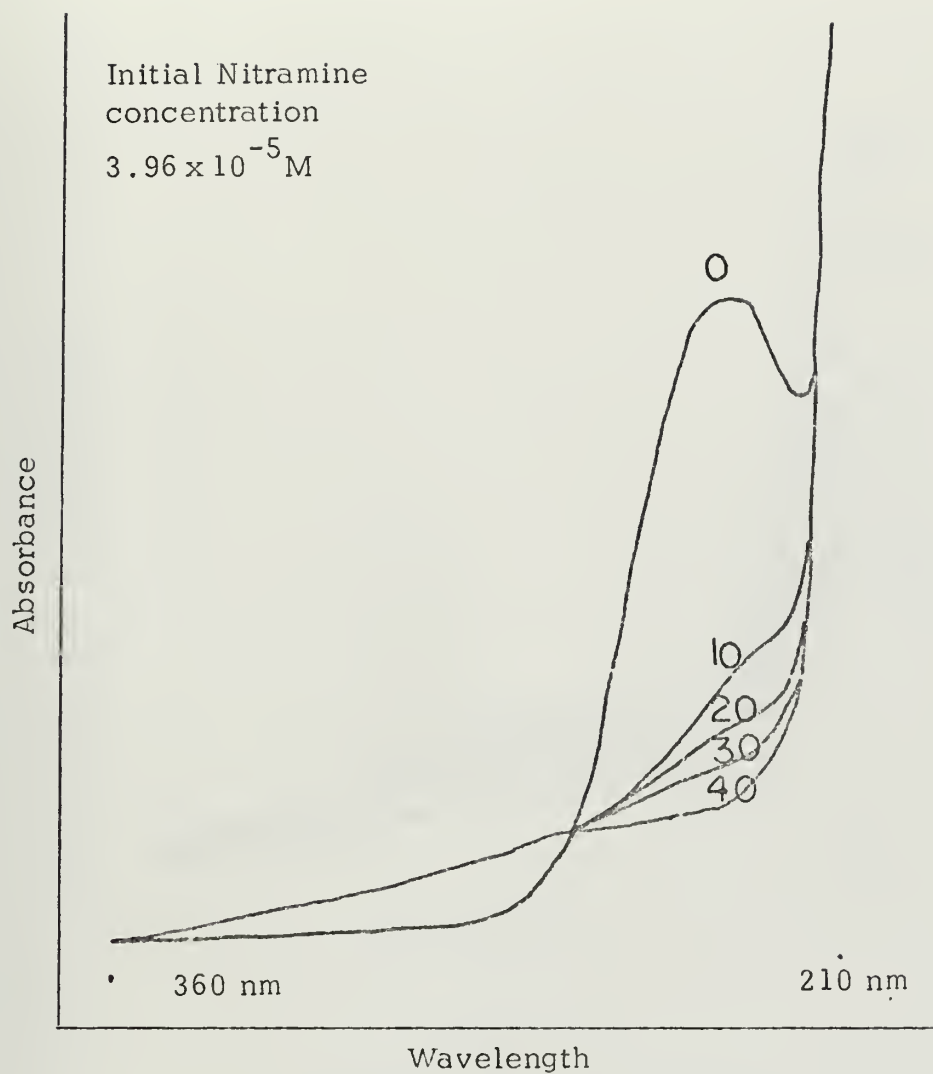


FIGURE 9.

ULTRAVIOLET ABSORBENCE

vs.

PHOTOLYSIS TIME (MIN.) FOR

N-NITROPYRROLIDINE AND

ACRYLONITRILE IN N-HEPTANE

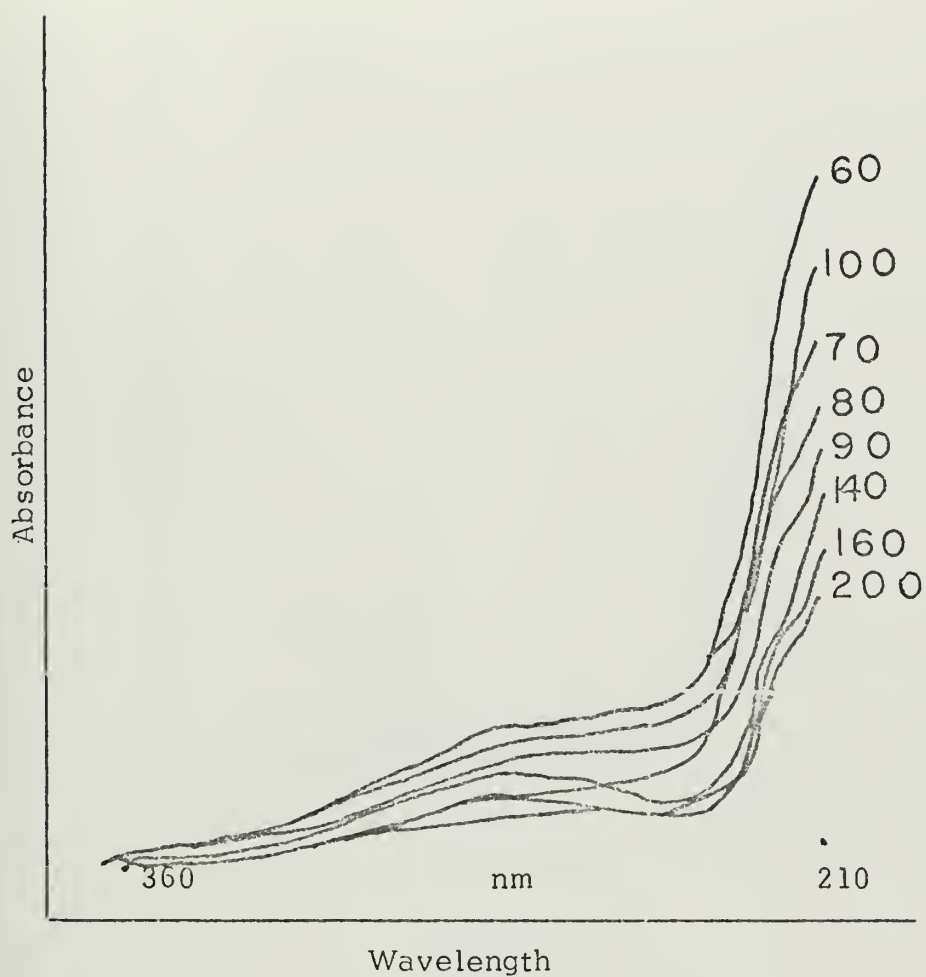


FIGURE 10.

ULTRAVIOLET ABSORBANCE

vs.

PHOTOLYSIS TIME (MIN.) FOR N-NITROPYRROLIDINE
AND ACRYLONITRILE IN N-HEPTANE

The change of the ultraviolet spectrum of N-Hydroxypyrrolidine in n-hexane with photolysis time is shown in Figure 11.

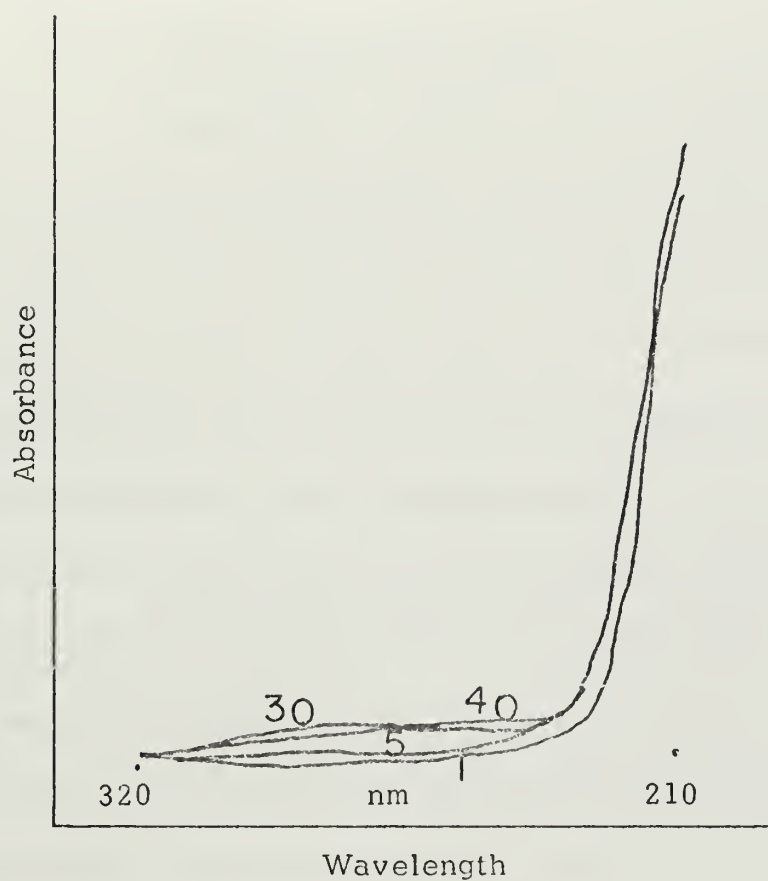


FIGURE 11.

ULTRAVIOLET ABSORBENCE

vs.

PHOTOLYSIS TIME (MIN.)

N-HYDROXYPYRROLIDINE IN N-HEXANE

D. ATTEMPTED ADDUCT FORMATION

1. Photo-adduct from Nitropyrrolidine Photolysis in

Acrylonitrile

a. Photolysis without a filter

The infrared spectrum of the starting materials was obtained. As photolysis progressed, samples were withdrawn and the ir spectra of these samples were obtained. As photolysis progressed, a sharp peak at 815 cm^{-1} was seen to grow in. This peak reached maximum intensity after 4 hours photolysis and then remained steady for at least the next 4 hours. After 24 hours photolysis, the peak had largely disappeared but it was present in the ir spectrum of the brown solid and yellow oil photolysis products which were obtained from acetone and ethanol extractions respectively. The product mixture did not yield any adduct from the activity 5 alumina column which was used in the column chromatographic treatment of the product mixture.

After the acrylonitrile had evaporated, the solid samples were redissolved in dimethylformamide. Gas chromatography on these samples was performed on the Bendix 2002 Gas Chromatograph. These gas chromatography runs showed 2 broad peaks with smaller peaks superimposed which appeared in the gas chromatograph between 100°C and 150°C . These peaks grew in intensity as photolysis time progressed. No other products were seen in the gas chromatography of the sample mixture.

The nmr spectrum of the product mixture after 45 hours photolysis showed a broad complex series of peaks at $\delta=2.5$ to $\delta=3.3$ (DSS).

b. Photolysis with the 230 nm filter

The nmr spectrum of the starting solution was obtained. This showed the normal nitramine peaks at $\delta=1.7$, a sextet, and 3.45, a triplet, based on DSS. The acrylonitrile was seen as a complex series of peaks from $\delta=5.1$ to 6.2.

After one hour photolysis, the nmr spectrum showed a broad flat peak at $\delta=3.2$ to 2.5 with 2 small peaks at $\delta=3.0$ and 3.1 superimposed. One hour's photolysis later these 2 peaks continued to grow with photolysis time. At the end of 5 hour's photolysis, 3 more peaks had grown in at $\delta=2.7$, 2.8 and 3.3 based on DSS.

After 10 hour's photolysis the nmr spectrum showed 2 peaks at $\delta=4.0$, and 4.2, and a complex group of 7 peaks at $\delta=3.3$ to $\delta=2.5$ (DSS). This complex group of peaks grew in intensity until at the end of 25 hour's photolysis the peak integration showed that approximately two-thirds of the nitramine had reacted to form the adduct.

An attempt to isolate the adduct from the product mixture failed.

c. Photolysis in 50/50 dioxane-acrylonitrile solution with 290 nm filter

The photolysis products were a yellow liquid and a cream solid as stated earlier in the experimental. The liquid turned to an orange-yellow color on storage for 24 hours in the dark. The solid

products were examined in the ir after each stage of treatment with heptane and CHCl_3 . No evidence of an adduct was found. The liquid phase also showed no evidence of the adduct.

2. Dark Phase Adduct of Photolysed Dinitropiperazine and Acrylonitrile

The nmr spectrum of the suspected adduct is shown in Figure 12. As mentioned earlier in the experimental, no adduct was recovered from the column chromatography attempt. The white crystalline product obtained showed an nmr spectrum indicated that it was probably dinitropiperazine. The melting point was 212°C after softening at 185°C to 190°C . The infrared spectrum was identical to that for pure dinitropiperazine except that the broad peak at 3400 cm^{-1} was much larger, a broad peak occurred at 1610 cm^{-1} and less detail was apparent in the region from 1300 cm^{-1} to 400 cm^{-1} .

E. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY STUDIES OF SUSPECTED INTERMEDIATES

1. N-Hydroxypyrrolidine

The nmr spectrum of N-hydroxypyrrolidine showed the following peaks relative to TMS: $\delta = 7.5$ Singleton - area 1; 2.65 Sextet - area 3; 1.15 Quintet - area 3.

There were also small peaks at $\delta = 7.0$ and near 1.45 due to small amounts of 2-pyrrolidone formed by air oxidation of the hydroxylamine.

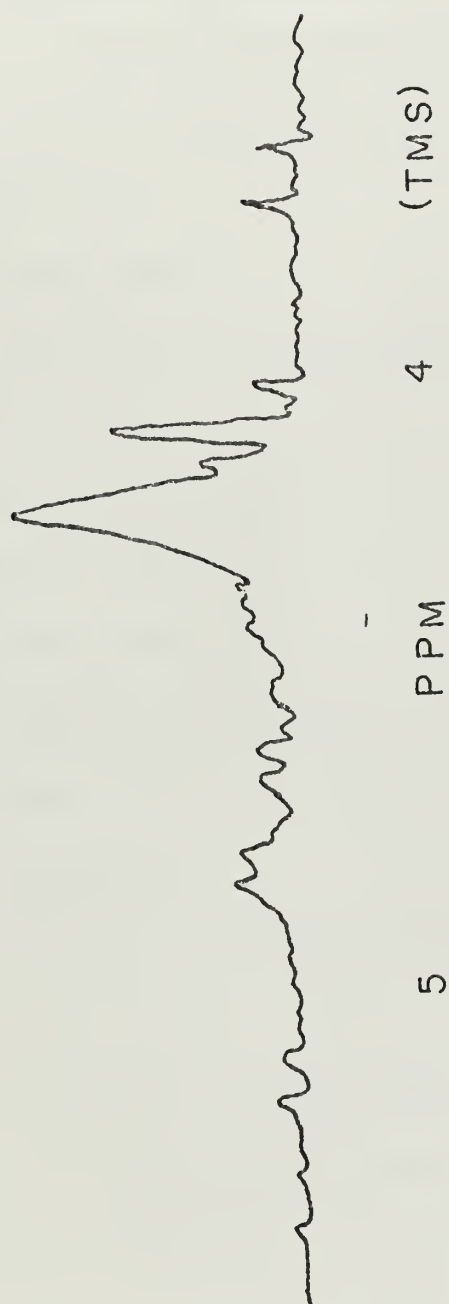


FIGURE 12.

NMR SPECTRUM OF DARK PHASE ADDUCT OF
PHOTOLYZED DINITROPIPERAZINE AND ACRYLONITRILE.

After 16 hours photolysis, the nmr spectrum showed the disappearance of the 2-pyrrolidone and a new broad peak had appeared at $\delta=4.2$. This peak disappeared after 24 hours at room temperature.

2. N-Hydroxypyrrolidine/N0

The only apparent difference in the nmr from the case above was that the peak at $\delta=4.2$ did not grow in as quickly during photolysis in the presence of N0.

3. 2-Pyrrolidone

The nmr spectrum of 2-pyrrolidone showed the following peaks relative to TMS:

$\delta = 7.0$ Broad Singlet - area 1

2.55 Triplet - area 4

1.45 Quintet - area 2.

After 16 hours photolysis, there was no detectable change in the nmr spectrum although the 2-pyrrolidone had visibly yellowed.

4. 1-Pyrroline

The nmr spectrum of the nitron in CDCl_3 showed the following peaks relative to TMS:

$\delta = 7.5$ Singlet - area 1

2.8 Quartet - area 4
(2 small)
(2 large)

1.4 Singlet - area 1

1.2 Quintet - area 4.5.

The 2 large peaks centered at $\delta = 2.8$ with reference to TMS were found to be at $\delta = 3.0$ and $\delta = 3.1$ in acetonitrile with DSS as a reference.

F. INFRARED SPECTRUM OF THE GASEOUS PHOTOLYSIS PRODUCTS OF DINITROPIPERAZINE

The infrared spectrum of the gaseous photolysis products showed the following peaks:

2900 cm^{-1}	Broad peak - moderate
2200 cm^{-1}	Broad peak - strong sharp spike at 2220
1620 cm^{-1}	Sharp peak - strong
660 cm^{-1}	Single peak - moderate
580 cm^{-1}	Single peak - strong

G. THERMAL SENSITIVITY OF DINITROPIPERAZINE

A plot of the weight loss of dinitropiperazine (log) against the reciprocal of temperature is shown in Figure 13. An Arrhenius calculation gives an energy of thermal decomposition or of sublimation of 2815 cal/mole.

H. IMPACT SENSITIVITY

The impact sensitivity testing of dinitropiperazine led to a value of 115 cm for the 50% point (50% chance of explosion).

I. NON-GASEOUS PHOTOLYSIS PRODUCT IDENTIFICATION

The infrared spectrum of X is included as Figures 14 and 15.

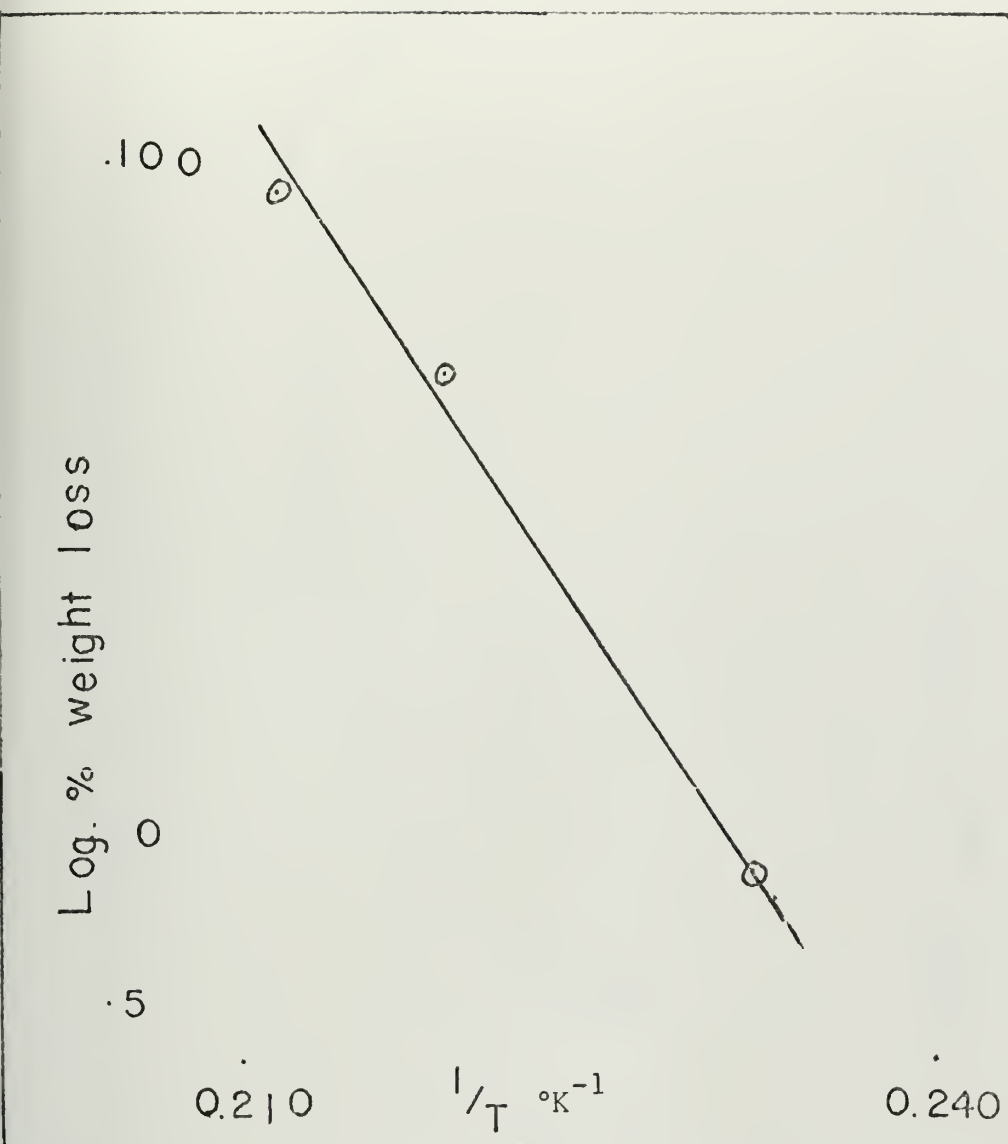


FIGURE 13.

THERMAL STABILITY OF N,N-DINITROPIPERAZINE.



FIGURE 14.
INFRARED SPECTRUM OF X 4000 - 1300 CM⁻¹.

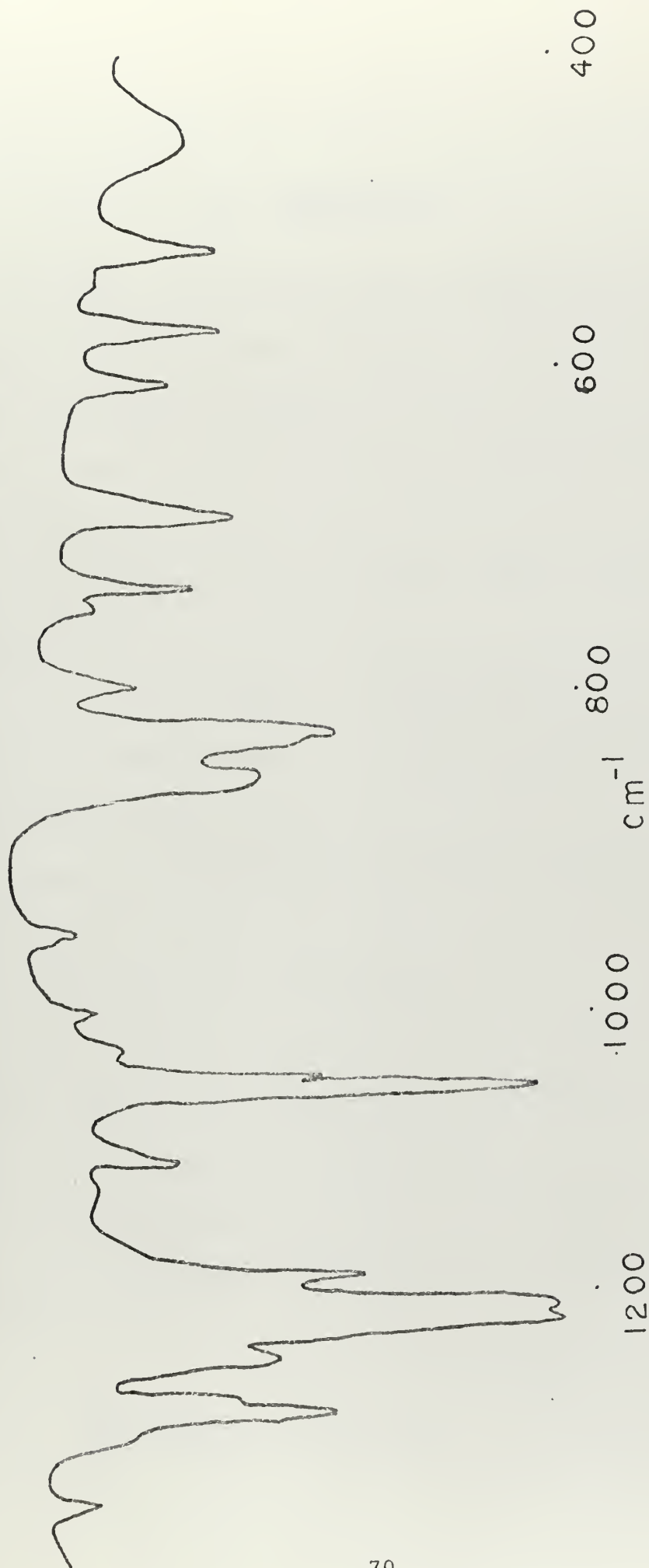


FIGURE 15.

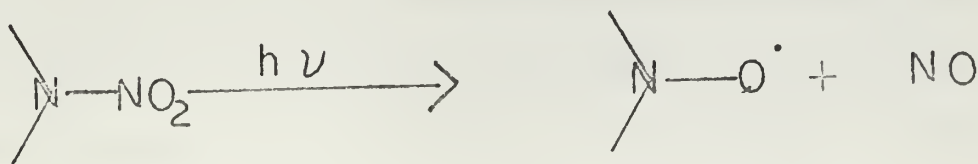
INFRARED SPECTRUM OF X 1300 - 400 CM⁻¹.

V. DISCUSSION

The electron spin resonance spectra obtained for the photolysis of nitramines makes it apparent that the first step of the photo-decomposition must involve the nitroxide. This step should also generate NO gas which would then be obvious in the mass spectra of the gaseous products. The very large peak of M/E 30 in the gaseous photolysis products spectra obtained when an effective filter was used during photolysis would seem to confirm this.

In the absence of a filter, the NO gas formed would take part in photochemical smog reactions and the relative amount of this gas would be expected to decrease. An increase in the relative amounts of N₂ (M/E 28) and O₂ (M/E 32) would be expected to accompany the decrease in the NO gas. This trend is seen in the mass spectra of N,N-dinitroperazine (Table III) and N-nitropyrrolidine (Table IV). Large peaks would also be expected at M/E 44 because of the production of N₂O and CO₂ from interaction of NO with itself and with stable organic products. This peak is seen in all of the mass spectra.

On the basis of the mass spectral and esr data, it seems likely that the first step of the photo-decomposition of nitramines must involve:



This is in contrast to the mechanisms proposed by Suryanarayana [6] and Torbit [8] for the photolysis of HMX. Since the nitroxide radical has been obtained from the photolysis of HMX, it would appear that the mechanisms they proposed for the photo-decomposition are incorrect as seen by these additional measurements.

Dupeyre [13] and Ingold [28] have suggested that the nitroxide formed should undergo a bimolecular reaction to give the nitron and the hydroxylamine. Upon further photolysis the hydroxylamine would be expected to give more nitroxide [10] and hence would not be isolable. The nitron, however, should be capable of being detected and trapped.

Synthesis of the nitron allowed determination of its ir, uv, and nmr spectra. If the nitron is, in fact, an intermediate, an absorption band, at 240 nm should be shown in the ultraviolet spectrum of the photolysis products. For a true intermediate, this band would be expected to grow in and then die out slowly as the nitron is formed and then converts photochemically to other products. This growth and decay of absorption at 240 nm is seen in Figures 9 and 10: "The photolysis of N-Nitropyrrolidine in n-Hexane." The nitron shows a strong absorption in the ir at about 1600 cm^{-1} . No great change was seen in the absorption at this wavelength during the photolysis of N-Nitropyrrolidine. This is not considered proof that the nitron was not present; however, since the uv spectra indicate that no large concentrations of nitron are achieved. It should also be noted that acrylonitrile was present during the photolysis studied in the ir in an effort to trap the nitron. The band

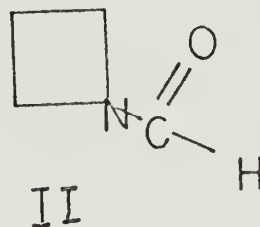
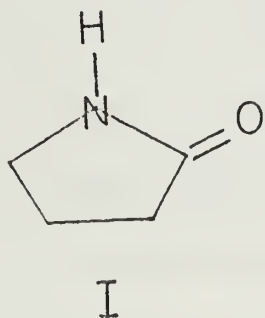
which grew in at 815 cm^{-1} does not come from the nitron but from another product which was later isolated. The nitron absorption at 1600 cm^{-1} appears strongly in the crude photolysis products in all cases.

In the nmr, peaks indicative of the nitron should be seen at $\delta = 3.0$ and 3.1 (DSS). These peaks, in the proper ratio, were seen in the nmr spectrum of the photolysis of N-nitropyrrolidine. It should be possible to trap the nitron by formation of the photo- or dark phase adduct of this intermediate with a compound containing a polarizable double bond [29]. This was in fact done by these authors and others, [15], [30], [31]. Ingold [28] found it very difficult to isolate these adducts. This author also had difficulty isolating adducts from the dark phase or photo-adduct formation attempts. Suspected adducts were seen in the nmr in the case of dinitropiperazine (dark phase adduct) and nitropyrrolidine (photo-adduct), but these could not be isolated. This is believed to be due to the presence of N_2O in the reaction mixture and to the separation techniques employed. N_2O should act as a catalyst in the polymerization of acrylonitrile and large amounts of what appeared to be polyacrylonitrile formed in some photo-adduct formation attempts. Such formation would be expected to inhibit the formation of adducts from acrylonitrile and the nitron. The use of activated alumina columns may have caused reversal of adduct formation. This is especially suspected in the case of the dark phase adduct of dinitropiperazine

where the ir and nmr spectra of products obtained from the column showed the probable presence of the mononitramine-mono-nitrone.

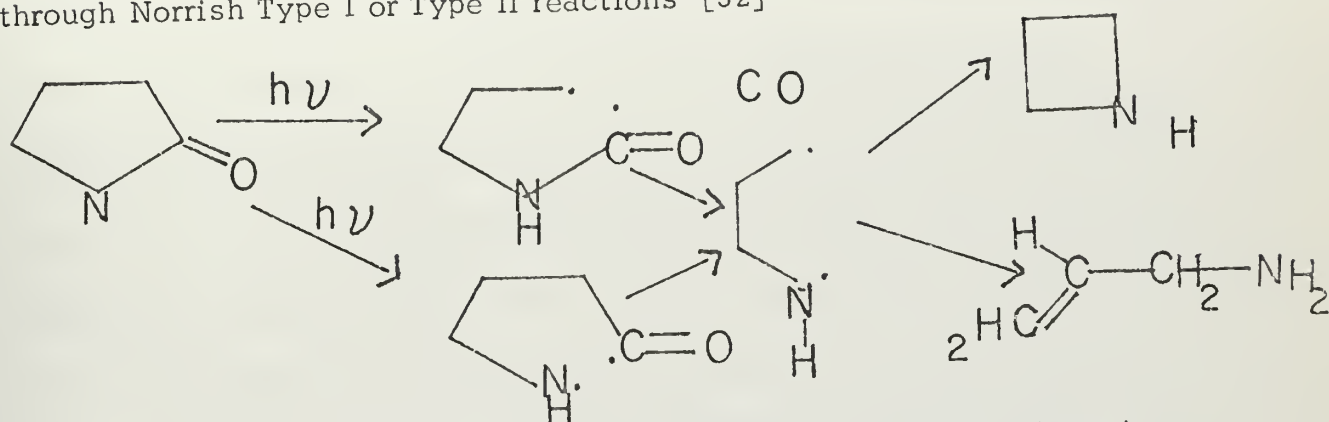
Kaminsky and Lamchen [15] have shown that photolysis of the nitrone leads to the oxaziridine. Since this compound does not absorb in the uv between 210 nm and 320 nm, the formation would be expected to be accompanied by a decrease in the absorption in this region. In the photolysis of N-nitropyrrolidine, a decrease in the absorption at 240 nm (nitrone) was observed. It was also observed that absorption at 260 nm increased with photolysis. This was shown to be due to the solvent and not attributable to the nitramine photolysis products. The oxaziridine cannot be isolated and was not synthesized independently. Thus its existence in the reaction path can only be suggested from the experience of others [15].

Kaminsky and Lamchen, in the same reference, also suggested the mechanism given in the Historical section of this report for the photolysis of nitrones. If this mechanism was correct, the final products would be 2-pyrrolidone, I, and N-formylazetidine, II.



The latter is unknown.

2-pyrrolidone would be expected to undergo further photolysis through Norrish Type I or Type II reactions [32]

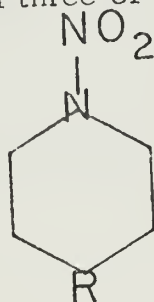


It is also possible that the 2-pyrrolidone formed would polymerize in the presence of free radicals resulting in a high molecular weight amino acid or amide.

The published mass spectra of 2-pyrrolidone [33] and azetidine [34] contain no peaks which do not occur in the gaseous photolysis products of N-nitropyrrolidine. If the Norrish mechanisms do in fact occur, the peaks at M/E 85, 57, 41, and 16 should occur in the mass spectrum of the photolysis products of N-nitropyrrolidine. These peaks do occur. Using the same mechanism applied to the case of N-nitropiperidine, the peaks at M/E 99, 71, 55, and 16 should and do occur. The mass spectrum in this case is also consistent with the presence of 2-piperidone [33] and pyrrolidine [34] as would be required in the Norrish rearrangements. The same concurrence of peaks does not occur in the case of 4-methyl-1-nitropiperidine. This may indicate a different mechanism in this case or a fortuitous coincidence in the case of N-nitropiperidine.

The solid reaction products may or may not be predicted by the mechanism above depending on the importance of polymerization in the mechanism. The yellow oil obtained from the photolysis of N-nitropyrrolidine had an ir spectrum very similar to that of yellow oils obtained from the photolysis of N,N-dinitropiperazine and HMX. Since very little information could be obtained below 1300 cm^{-1} due to the scarcity of peaks in this region, the actual identity of these oils could not be obtained spectroscopically and no further identification was attempted. It is of interest though, that a yellow oil obtained from purification of 1-pyrroline had an identical ir spectrum from 4000 cm^{-1} but lacked the sharp, large peak which occurred at 1340 cm^{-1} in oils obtained from the nitramines.

The occurrence of X as a reaction product for N,N-dinitropiperazine, N-nitropyrrolidine, and N-nitropiperidine may be a key to the mechanism beyond the nitron. All three of these nitramines have the same structure given below:



for N,N-dinitropiperazine

$R = \text{N}-\text{NO}_2$

N-nitropyrrolidine

$R = \text{bond between adjacent carbons}$

N-nitropiperidine

$R = \text{CH}_2$

X may thus be a product which requires one of the following structures for formation:

where $a, b, m, n = 0, 1, 2$ independently. An examination of the solid photolysis products of HMX failed to yield X. Examination of the ir spectrum of X [35], [36], leads to the belief that it may be an amide. The absence of a band near 1700 cm^{-1} is, however, suspect. A comparison of the characteristic regions of the ir spectra of X and sorbitol reveals a very great similarity. This leads to the possibility that X is a polyhydroxy compound. The negative Schiff's test on the periodate treated solution of X tends to lead to the belief that if it is a polyol, the hydroxyl groups are not adjacent. On the basis of the information from the ir spectrum, the inability to obtain an nmr spectrum, the lack of detail in the uv spectrum and the poor melting point available, it is not possible to assign any definite structure to X.

On the basis of the evidence obtained spectroscopically and the work of earlier authors, the following mechanism for the photolysis of N-nitropyrrolidine is suggested.



BIBLIOGRAPHY

1. Carignan, Y. P., and Satriana, D. R., "Differential Thermal Analysis of Nitramines, Amine Salts, and Guanidine Derivatives," Journal of Organic Chemistry, v. 32, p. 285-289, February 1967.
2. Suryanarayana, B., Autera, J.R., and Graybush, R.J., "Thermal Degradation of Secondary Nitramines: A Nitrogen -15 Tracer Study of HMX (1, 3, 5, 7-Tetranitro-1, 3, 5, 7-Tetraazacyclooctane)," Chemistry and Industry, v. 52, p. 2177-2178, December 1969.
3. Maksinov, Yu.Ya., "Thermal Decomposition of Hexogen and Octogen," Transcripts of the Moscow Chemical and Technological Institute, v. 53, p. 73-84, 1967.
4. Robertson, A.J.B., "Thermal Decomposition of Explosives II. Cyclotrimethylenetetranitramine (Cyclonite) and Cyclotetramethylenetetranitramine," Transactions of the Faraday Society, v. 45, p. 85-93, January 1949.
5. Flournoy, J.M., "Thermal Decomposition of Gaseous Dimethylnitramine," Journal of Chemical Physics, v. 36, p. 1106-1107, February 1962.
6. Suryanarayana, B., Graybush, R.J., and Autera, J.R., "Effect of Ultraviolet Irradiation on Phase Transformations in Octahydro-1,3, 5,7-Tetranitrotetrazocine Polymorphs," Molecular Crystals, v. 2(4), p. 373-377, 1967.
7. Maycock, J.N., Verneker, V.R.Pai, and Lochte, W., "Physico-Chemical Properties of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX) II. Spectra and Ultraviolet Radiation Damage Phenomena," Physica Status Solidi, v. 35, no. 2., p. 849-860, October 1969.
8. Torbit, J.R., "The Photochemical Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX)," Thesis, U.S. Naval Postgraduate School, April 1970.
9. Darnez, C., Paviot, J., and Cherville, J., "Etude par R.P.E. de la Radolyse de la Cyclotrimethylene Trinitramine," Journal de Chimie Physique et de Physio-chimie biologique, v. 66, p. 2016-2017, 1969.

10. Windle, J.J., Kuhnle, J.A., and Beck, B.H., "ESR Study of Inter-conversion of Piperidine Iminoxyls," Journal of Chemical Physics, v. 50(6), p. 2630-2641, March 1969.
11. Buchachenko, A.L., Stable Radicals, p. 135-141, Consultants Bureau, 1965.
12. Morrison, A., and Davies, A.P., "Mass Spectrometry of Piperidine Nitroxides - A Class of Stable Free Radicals," Organic Mass Spectrometry, v. 3, p. 353-366, 1970.
13. Dupeyre, R.M., and Rassat, A., "Nitroxides XIX Norpseudo-pelletierine N-Oxyl, A New Stable Free Radical," Journal of the American Chemical Society, v. 88(13), p. 3180-3181, July 1966.
14. Keana, J.F.W., Dinerstein, R.J., and Friedhelm, B., "Photolytic Studies on 4-Hydroxy-2,2,6,6,-Tetramethylpiperidine-1-Oxyl, a Stable Nitroxide Free Radical," Journal of Organic Chemistry, v. 36, p. 209-211, 1971.
15. Kaminsky, L.S., and Lamchen, M., "Nitrones III. Photolysis of Cyclic Nitrones," Journal of the Chemical Society (C), p. 2295-2299, 1966.
16. Kinstle, T.H., and Stam, J.G., "Mechanisms of Mass Spectral Fragmentations of Nitrones," Chemical Communications (4), p. 185-186, 1968.
17. George, M.V., and Wright, G.F., "The Steric Conformations of Nitro- and Nitro-bis-piperazines," Journal of the American Chemical Society, v. 80, p. 1200-1204, 1957.
18. Coburn, M.D., and Ungnade, H.E., "Synthesis and Structure of the N-Nitropyrrolidones (1)," Journal of Heterocyclic Chemistry, v. 2, no. 3, p. 308-309, 1965.
19. Spath, E., and Lintner, J., "Formation of Lactams from Lactones," Chemische Berichte, v. 69B, p. 2727-2731, 1936.
20. Ruppert, W., German Patent 1,004,191 March 1957, reported in Chemical Abstracts, v. 54, p. 584, 1960.
21. Anderson, G.W., Zimmerman, J.E., and Callahan, F.M., "The Use of N-Hydroxysuccinimide in Peptide Synthesis," Journal of the American Chemical Society, v. 86, p. 1839, May 1964.

22. Bonnet, R., Ho, S.C., and Raleigh, J.A., "Studies in the Pyrroline Series V, 3,3-Dimethyl-1-Pyrroline-1-Oxide," Canadian Journal of Chemistry, v. 43, 1965.
23. Thesing, J., and Sirrenberg, W., "Cyclische Nitrone, IV. Darstellung und Eigenschaften des Δ^1 -Pyrroline-N-Oxyds," Chemische Berichte, v. 92, p. 1749, 1959.
24. United States Naval Postgraduate School Technical Report no. 16, The Effect of Explosive Mixtures Upon Impact Sensitivity, by J. E. Sinclair, p. 4-17, March 1957.
25. Bodnar, J. W., "Photochemistry of Nitramines, I: Preparation of Nitroxides in Solution and in Situ in Single Crystals," Thesis, U. S. Naval Postgraduate School, June 1971.
26. Cheronis, N.D., and Entrikin, J.R., Semimicro Qualitative Organic Analysis, 2d ed., p. 202, Interscience Publishers, 1957.
27. Calvert, J.G. and Pitts, J.N., Jr., Photochemistry, p. 214, Wiley, 1966.
28. Adamic, K., Bowman, D.F., Gillan, T., and Ingold, K.U., "Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy I. Self-Reactions of Diethyl Nitroxide Radicals," Journal of the American Chemical Society, v. 93, no. 4, p. 902-908, February 1971.
29. Delpierre, G.R., and Lamchen, M., "Nitrones, Part I. Cycloaddition of Unsymmetrical Olefins to the 1-Pyrroline-1-Oxides," Journal of the Chemical Society, p. 4693-4701, 1963.
30. Lamchen, M., and Mittag, T.W., "Nitrones Part VII. The Photochemistry and Cycloaddition of a Monocyclic α -Dinitrone," Journal of the Chemical Society (C), p. 1917-1921, 1968.
31. Brown, C.W., Marsden, K., Thorold-Rogers, M.A., Tylor, C.M.B., and Wright, R., "The Condensation of Nitrones and Olefins," Proceedings of the Chemical Society, p. 254, 1960.
32. Hine, J., Physical Organic Chemistry, 2d ed., p. 417, McGraw-Hill, 1962.
33. Duffield, A.M., Budzikiewicz, H., and Djerassi, C., "Mass Spectrometry in Structural and Stereochemical Problems, LVIII. A Study of Fragmentation Processes of Some Lactams," Journal of the American Chemical Society, v. 86, p. 5536-5541, December 1964.

34. Gallegos, E.J., and Kiser, R.W., "Electron Impact Spectroscopy of the Four and Five Membered Heterocyclic Compounds Containing Nitrogen, Oxygen, and Sulphur," Journal of Physical Chemistry, v. 66, p. 136-145, January 1962.
35. Silverstein, R.M., and Bassler, G.C., Spectrometric Identification of Organic Compounds, p. 78-108, Wiley, 1968.
36. Ewing, G.W., Instrumental Methods of Chemical Analysis, 2d.ed., p. 78-79, McGraw-Hill, 1960.

INITIAL DISTRIBUTION LIST

	No. Copies
1. Defense Documentation Center Cameron Station Alexandria, Virginia 22314	2
2. Library, Code 0212 Naval Postgraduate School Monterey, California 93940	2
3. Assoc. Professor C. F. Rowell, Code 5413 Department of Material Science and Chemistry Naval Postgraduate School Monterey, California 93940	1
4. LT Harry Whittaker 3470 Carre Lormeau Ste. Foy, Quebec 10 Quebec, Canada	1
5. Maritime Combat Systems Canadian Forces Headquarters Ottawa 4, Ontario, Canada	1

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

ORIGINATING ACTIVITY (Corporate author)

Naval Postgraduate School
Monterey, California 93940

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

REPORT TITLE

Photochemistry of Nitramines II Stoichiometry, Intermediates and Products

DESCRIPTIVE NOTES (Type of report and, inclusive dates)

Master's Thesis; June 1971

AUTHOR(S) (First name, middle initial, last name)

Harry Whittaker

REPORT DATE

June 1971

7a. TOTAL NO. OF PAGES

85

7b. NO. OF REFS

36

3a. CONTRACT OR GRANT NO.

b. PROJECT NO

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Naval Postgraduate School
Monterey, California 93940

13. ABSTRACT

This investigation was concerned with the photochemical decomposition of nitramines, particularly N-nitropyrrolidine and N, N-dinitropiperazine. Photolyses were carried out in solution and in the solid state. Intermediates were identified by spectroscopic studies and by synthesis.

On the basis of the intermediates, products, and spectroscopy of products, a mechanism for the photochemical decomposition of N-nitropyrrolidine was postulated.

200171
100172

20829
21991

Thesis
W564
c.1

Whittaker 128252
Photochemistry of
nitramines II stoi-
chiometry, interme-
diates and products.
200171
100172
20829
21991

Thesis
W564
c.1

Whittaker 128252
Photochemistry of
nitramines II stoi-
chiometry, interme-
diates and products.

thesW564

Photochemistry of nitramines II stoichio



3 2768 001 95093 4

DUDLEY KNOX LIBRARY